

ON THE STRUCTURE OF HUMIC ACIDS

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I. Introduction

About four years ago, the Research Council of Alberta initiated a series of coordinated, continuing studies from which several important inferences about the structure of humic acids can now be drawn. The present paper is intended briefly to review these studies and to outline those features of the humic acid molecule which can, in our view, be formulated with some confidence.

Almost all experimental data cited in the following sections were duplicated by working with humic acids derived from a weathered N. Dakota lignite*, and a weathered subbituminous coal occurring at Sheerness, Alberta. However, since these two materials displayed virtually indistinguishable behaviour, no attempt is here made to differentiate between the respective sets of results; and it is, in fact, tentatively contended that coal-derived humic acids may be regarded as chemical entities whose main structural features are essentially independent of their sources of origin.

II. The Molecular Weights of Humic Acids

In view of the then prevailing uncertainty about the size of the humic acid molecule, the initial study was concentrated upon renewed attempts to determine significant molecular weights (1). For convenience, a cryoscopic technique was used for this purpose, but in place of conventional solvents (e.g. acetamide, 2), sulfolane was employed. This solvent (3) offered several distinct and important advantages. It possesses an unusually high cryoscopic constant ($K = 65.5$ degrees - kg per mole); it affords a ready means for dissolving humic acids and completely drying the resultant solution; and it appears to eliminate disturbing effects due to solute association and/or dissociation. Generally ideal behaviour of sulfolane could, for example, be demonstrated by experiments with solutions containing such diverse compounds as benzoic acid, β -naphthalene sulfonic acid and biphenyl: in all instances, K proved to be quite independent of solute concentrations over the molality range 0.01 to 0.10. Direct evidence for the absence of association of solute molecules in a sulfolane solution could also be obtained from infrared data - notably from analysis of the -COOH and -OH stretching frequencies of simple analog compounds.

* Commercially marketed as Baroid Carbonox.

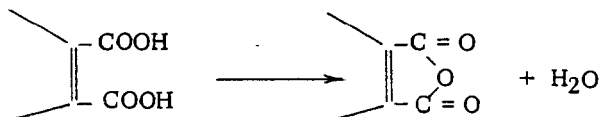
Using the sulfolane method with a series of carefully fractionated humic acids, molecular weights ranging to ca. 10,000 were recorded (1) and broadly confirmed by sedimentation velocity measurements.

It is of some interest to note that while molecular weights of the order of thousands stand in marked contrast to previously reported cryoscopic data, they are in general agreement with semi-quantitative diffusion measurements reported, *inter alia*, by Dryden (4).

III. The Disposition of Peripheral Functional Groups

Estimates of the concentrations of functional groups by established methods (5, 6) yielded results comparable to those reported for humic acids by other laboratories. Typical values (7) were: $-\text{OCH}_3$ 1.7, phenolic $-\text{OH}$ 2.7, and $-\text{COOH}$ 4.3 milliequivalents per gram. More detailed studies, however, permitted some refinement of these data and, more important, inferences about the disposition of certain functional groups around the molecular periphery.

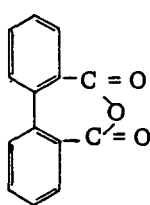
When solutions of humic acid in sulfolane were heated to $170^\circ - 200^\circ\text{C}$ under reduced pressure and subsequently examined by infrared spectroscopy, the intensity of the original carboxyl carbonyl absorption at 1735 cm^{-1} was found to be greatly reduced, and two new bands centring at 1850 and 1785 cm^{-1} were observed (Figure 1). Since identical absorptions were seen in the infrared spectra of phthalic and 1,2-naphthalic anhydrides formed in hot sulfolane, these bands were assigned to 5-membered ring anhydrides of humic acid, i.e. to simple dehydration products of the type,



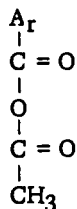
and it was concluded that a substantial number of $-\text{COOH}$ groups in the humic acid molecule occupy mutually adjacent sites. Six- or 7-membered ring anhydrides could be ruled out because of their infrared absorption at quite different frequencies, and still larger cyclic anhydrides were discounted by the rather narrow band separation generally seen in the spectra of such compounds.

When, on the other hand, humic acid is refluxed with acetic anhydride, a more complex situation is created. The intensity of the original $-\text{COOH}$ band is again greatly reduced, but now at least four new bands (at 1850 , 1820 , 1785 and 1745 cm^{-1}) are found; and the 1785 cm^{-1} band is, compared with the 1850 cm^{-1} absorption in the same spectrum, substantially more intense than in the spectrum of humic anhydride formed in hot sulfolane (Figure 1).

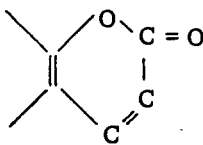
On the assumption that reaction with acetic anhydride forms, among other products, the same anhydrides as are produced by heating sulfolane solutions of humic acid, cyclic 5-membered ring anhydrides were therefore now supposed to account for only a part of the 1785 cm^{-1} absorption, and a number of theoretically possible contributing structures were examined. Among these were cyclic anhydrides of type (I), open chain anhydrides, including mixed anhydrides (II), lactones (III), esters (presumably of the phenolic acetate type IV), and esters and/or anhydrides formed between molecules of humic acid.



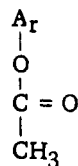
I



II



III



IV

The results, partly based upon extended experimentation with exhaustively methylated, alkali-hydrolyzed humic acid and acetyl analyses (8) led to the following conclusions(7):

(a) Approximately 80% of all -COOH groups existing in humic acid occupy sites permitting the formation of cyclic ring anhydrides.

(b) Approximately one-fifth of all -COOH groups form linear mixed anhydrides when humic acid is reacted with acetic anhydride (but not in sulfolane) and must therefore exist as isolated groups or in odd-numbered groups on adjacent ring sites.

(c) Of the several, theoretically possible 6- and 7-membered ring anhydrides, only anhydrides of the diphenic type (I) are consistent with experimental evidence.

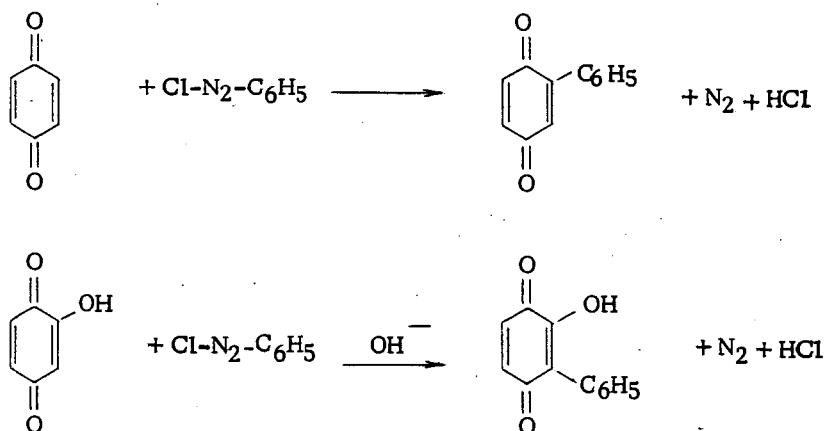
Since a part of the strong 1785 cm^{-1} band in the spectra of humic anhydrides formed by reaction with acetic anhydride can also be ascribed to esters — and in particular to esters of polyfunctional phenols — it is tentatively further thought possible that a proportion of the total -OH content of humic acid may occur as groups of 2 or 3 -OH residues on the same ring or condensed aromatic nucleus. This view is, however, subject to rather severe limitations since -OH residues located ortho or para to each other would undoubtedly be converted to quinones by the conditions under which humic acids form.

IV. Quinone Structures

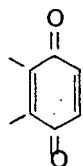
When humic acid is reacted with diazotized sulfanilic acid, a water-soluble derivative forms through introduction of $-N=N-C_6H_4-SO_3H$ and/or $-C_6H_4-SO_3H$. Both mechanisms, i.e. interaction with phenolic structures or with quinones, are consistent with infrared spectral evidence in that both would lead to the new absorptions indicative of the presence of sulfonic groups which are observed (Figure 2b); but since the former requires introduction into the humic acid molecule of two nitrogen atoms per additional sulfur atom (which analysis shows not to occur to any significant extent), it has been concluded that the dominant reaction involves a free radical attack on quinones at an available position.

Proceeding from this recognition, an interesting route to further elucidation of the structure of humic acid can be developed (9).

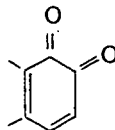
Of the two most probable theoretical free radical mechanisms by which a $-C_6H_4-SO_3H$ group is introduced into the humic acid molecule, one — a Gomberg reaction — must be ruled out on evidence offered by Gomberg and Pernert (10), Grieve and Hey (11), and Walling (12). There remain therefore only interactions of the type



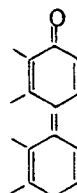
from which it follows that humic acid molecules reacting with the diazonium salt must contain one or more of the basic structures V, VI and VII.



V



VI



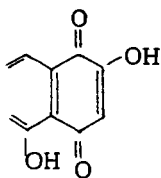
VII

Now, the possible existence of these (or similar) entities in humic acid has been recognized for some years. But more unequivocal information about them has now been obtained by infrared studies on methylated* and subsequently acetylated humic acids. Of particular importance was the existence in the spectra of these compounds of a fairly intense absorption band at 1660 cm^{-1} (Figure 2d), i.e. at the same frequency at which a wide range of relatively simple quinones (cf. Table I) show a diagnostic absorption. If this observation is viewed against the background of polarographic evidence (13) and x-ray diffraction data (14) — which preclude polycondensed ring systems of more than 4-5 rings in low and medium rank coals — it can be concluded with reasonable safety that while simple benzoquinones cannot be postulated, possible structures could include OH-substituted naphthoquinones and anthraquinones as well as more complex systems containing heterocyclic oxygen. Detailed examination of the infrared spectra obtained in these laboratories leads, in short, to the conclusion that structures VIII and IX appear to be the simplest consistent with presently available evidence.

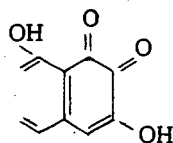
Table I. Carbonyl stretching frequencies of quinones

Compound	Frequencies cm^{-1}	Phase
1,4-Benzoquinone	1665	Mull
1,2-Benzoquinone	1669	CCl_4
1,4-Naphthoquinone	1662	Mull
1,2-Naphthoquinone	1678	CCl_4
Anthraquinone	1671	Mull
9,10-Phenanthraquinone	1670	Mull
Anthrone	1654	Mull
Bianthrone	1657	Mull
Bianthranyl	1656	Mull
Anthanthrone	1650	Mull
Dibenzypyrenequinone	1645	Mull
3,8-Pyrenequinone	1636	Mull
3,10-Pyrenequinone	1640	Mull
Dibenzanthrone	1645	Mull
isoViolanthrone	1646	Mull
Pyranthrone	1642	Mull
Helianthrone	1642	Mull
1,2-Chrysenequinone	1661	Mull
1,2-Benzanthra-9,10-quinone	1664	Mull
1,2,3,4-Dibenzanthraquinone	1662, 1749	Mull
1,2,5,6-Dibenzanthraquinone	1652	Mull
3,10-Perylenequinone	1650	Mull

- * Initial methylation was designed to block all readily accessible hydroxy groups of phenols and carboxyls and thereby to avoid interference due to acetate esters and anhydrides in the 1800 and 1740 cm^{-1} regions of the infrared spectra.



VIII

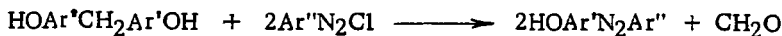


IX

It is, in this connection, noteworthy that estimates of the concentration of quinones in humic acid (9) by several different techniques yielded values of the order of 0.8 ± 0.2 milliequivalents/gm. The corresponding concentration of hydrogen-bonded quinones, which was derived from acetyl determinations on the assumption that each quinonoid oxygen is H-bonded to one phenolic -OH that can in turn be acetylated by acetic anhydride, was found to be 0.63 milliequivalent/gm. (and thus in good agreement with previously reported values; 15, 16, 17, 18).

An estimate of the carboxyl carbonyl:quinone ratio was obtained from the relative intensities of the 1660 and 1735 cm^{-1} absorptions on the assumption that the relationship between these bands was similar to that prevailing in the infrared spectrum of 2-(p-carboxyphenyl)-1, 4-naphthoquinone (which was chosen as a suitable model compound - Figure 2e). This ratio was found to be 14 as compared with 6 calculated from analytical data. While this discrepancy is large, it is, in view of the obvious inaccuracies entailed in the estimation via infrared spectra, not excessive.

With respect to the water-solubility induced in the humic acid derivative by reaction with the diazonium salt it might also usefully be noted that this appears only partly to arise from the introduction of sulfonic acid residues; a contributory factor seems to be cleavage of $-\text{CH}_2-$ bridges and the consequent reduction in molecular size. In support of this view attention is drawn to the identification of formaldehyde among the reaction products. The formative step for this would be



Recent experiments in these laboratories have shown that coals can undergo similar reaction with diazotized sulfanilic acid, but that the yield of water-soluble products decreases rapidly with increasing rank. While a lignite (C = 71% d.a.f.) showed after two treatments a ca. 80-90 per cent conversion, two subbituminous coals (C = 74 and 80% resp.) yielded after several treatments only about 50 to 70 per cent water-soluble derivatives, and a bituminous coal (C = 87%) proved almost wholly unreacted.

An alternative technique now actively being explored, i.e. sulfo-methylation (19,20,21) by means of $\text{CH}_2=\text{O}$ and NaHSO_3 leading to the addition of $-\text{CH}_2\text{SO}_3\text{H}$ to the aromatic nuclei, has been shown to produce analogous results (and, if anything, to be even more strongly affected by coal rank). It is, however, considered that yields of water-soluble products obtainable by this reaction, or by reaction with a diazonium salt, can be significantly increased by mild preliminary oxidation of the coal.

V. The Skeletal Structure

From measurements of the viscosities of humic acid solutions it has been concluded that humic acids may resemble flexible, linear polyelectrolytes (22). This conclusion, however, is considered untenable since humic acids show surprising stability in high-intensity ultrasonic fields (23); even prolonged exposure at frequencies up to 2 mc/s and intensities up to ~ 10 watts/cm² have failed to induce molecular rupture. Since the molecular weights of the test samples exceeded 5,000, i.e. a size at which linear molecules would degrade, it has, in the light of x-ray diffraction evidence, been postulated that the most probable skeletal structure involves relatively small (3-4 condensed ring) aromatic systems interlinked by mixed $-\text{O}-$ and $-\text{CH}_2-$ bridge structures. Linkage by $-\text{O}-$ only was ruled out by the fact that pyrolysis of humic acids yields considerable quantities of tarry matter (and, subsequently, by the detection of $\text{CH}_2=\text{O}$ as a by-product of reaction with diazonium salts, cf. above).

To test this general concept in detail, and to develop means for quantitative estimation of $-\text{CH}_2-$ and $-\text{O}-$ concentrations, current studies in these laboratories are directing attention to reactions of humic acid with (a) BF_3 in phenol, and (b) Na in liquid ammonia.

Interactions between coal and BF_3 -phenol have recently been reported by Heredy and Neuworth (24) who found 60-80% conversion of a high volatile bituminous coal into soluble products, presumably by the rupture of methylene bridges between aromatic nuclei. We have now observed humic acids to be completely soluble in this reagent mixture. The reaction appears to be accompanied by considerable molecular degradation* and several direct comparisons are possible between Heredy and Neuworth's and our results. Thus:

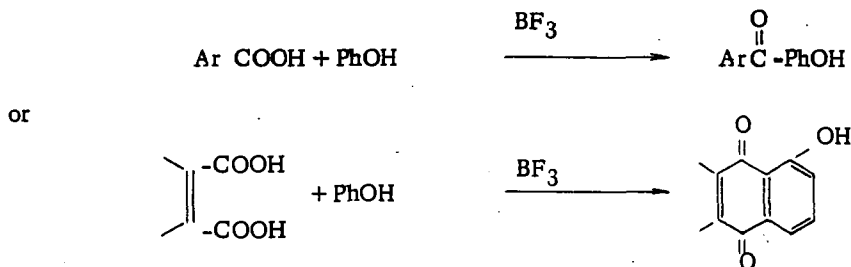
(a) A considerable increase in weight results from interaction between humic acid and BF_3 -phenol (e.g. from 13.6 to 29.0 gm); this indicates a combined phenol content of 53.2% which compares with a value of 55.7% reported by Heredy and Neuworth for one of their fractions.

(b) The reacted, BF_3 -phenol-soluble humic acid is, like the soluble coal fraction (above) of Heredy and Neuworth, soluble in methanol.

* Quite low molecular weight crystalline reaction products have been isolated from the mixture and tentatively identified by us. Details will be published elsewhere in due course.

(c) The phenolic -OH concentration in reacted humic acid amounts to ca. 5.1 milliequivalents/gm (as compared with 4.3 milliequivalents/gm for the reacted coal fraction referred to in (a) above).

A particularly noteworthy observation is that the carboxyl groups initially present in humic acid are completely eliminated by reaction with BF_3 -phenol — probably as a result of BF_3 -catalyzed condensation of the type (26):



If a scheme of this form is tentatively accepted, the further assumption that each $-\text{CH}_2-$ group reacts with two molecules of phenol leads to the conclusion that methylene bridges occur in humic acid at the rate of one per every ~ 200 molecular weight units. An assumption that each $-\text{CH}_2-$ reacts with a single phenol molecule (24) would halve this estimate. If it is (quite reasonably) supposed that a proportion of $-\text{CH}_2-$ will survive the oxidation processes by which coal is converted into humic acid, even the first estimate is in good agreement with a value of ca. one $-\text{CH}_2-$ per every 100 molecular weight units in coal (26).

The interest attaching to reactions with sodium in liquid ammonia arises primarily from the ability of this reagent mixture to cleave aromatic ether linkages which are, for various reasons, presumed to exist in humic acid (and coal). Detailed studies of this aspect in our laboratories are still in their initial stages; but it is worth noting that while reaction between humic acid and Na-NH_3 leaves a substantial residue of insoluble material, the derivative obtained from reaction with BF_3 -phenol becomes completely soluble in acetone. We are tentatively inclined to the view that this differentiation lends some support to the existence of mixed $-\text{CH}_2-$ and $-\text{O}-$ bridges in the parent molecule.

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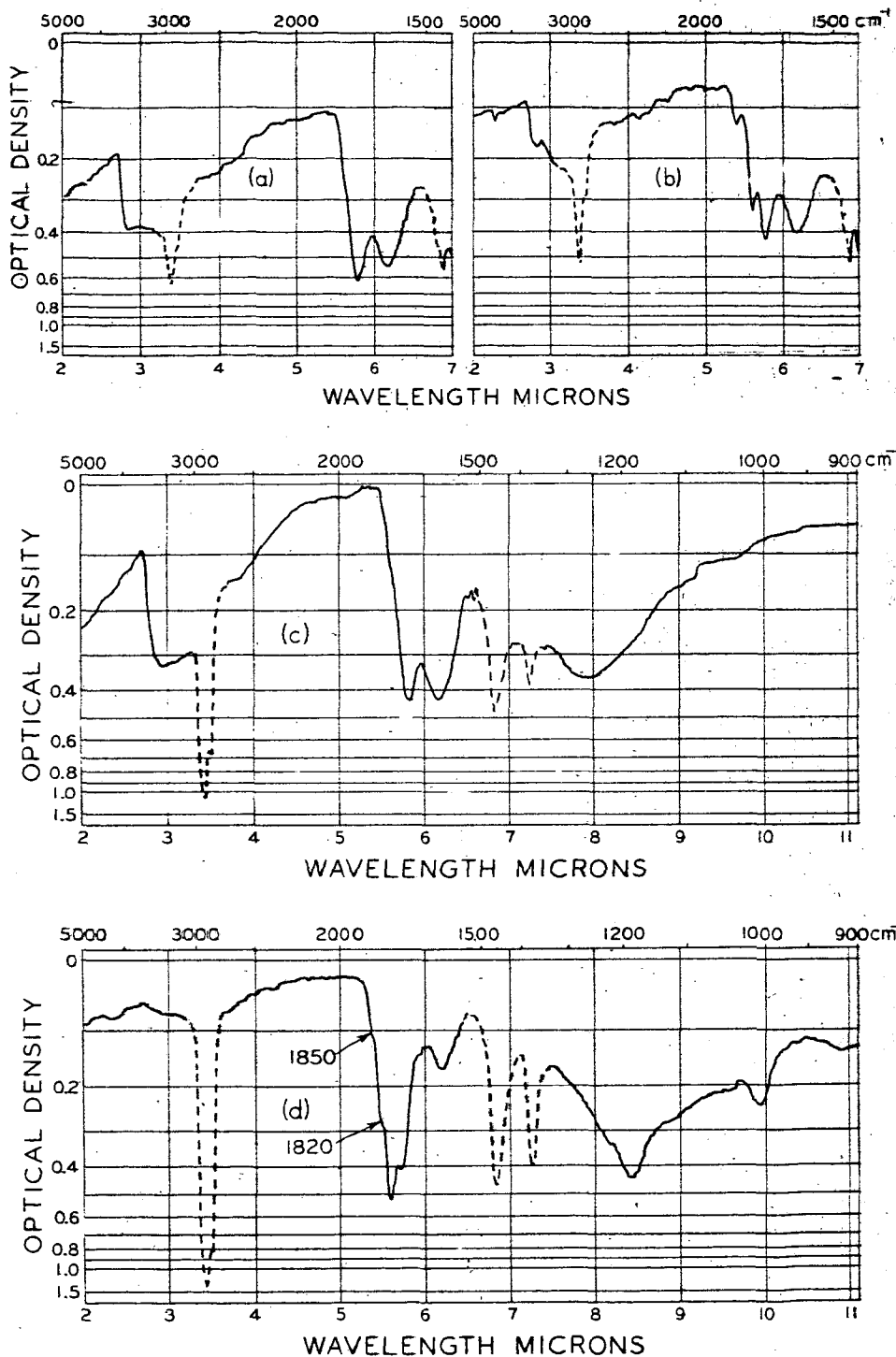


FIGURE 1. Humic acids and derivatives

- (a) parent humic acids (sulfolane mull). (c) parent humic acid (Nujol mull).
 (b) humic acids heated in sulfolane (d) humic acids treated with boiling
 (sulfolane mull). acetic anhydride (Nujol mull).

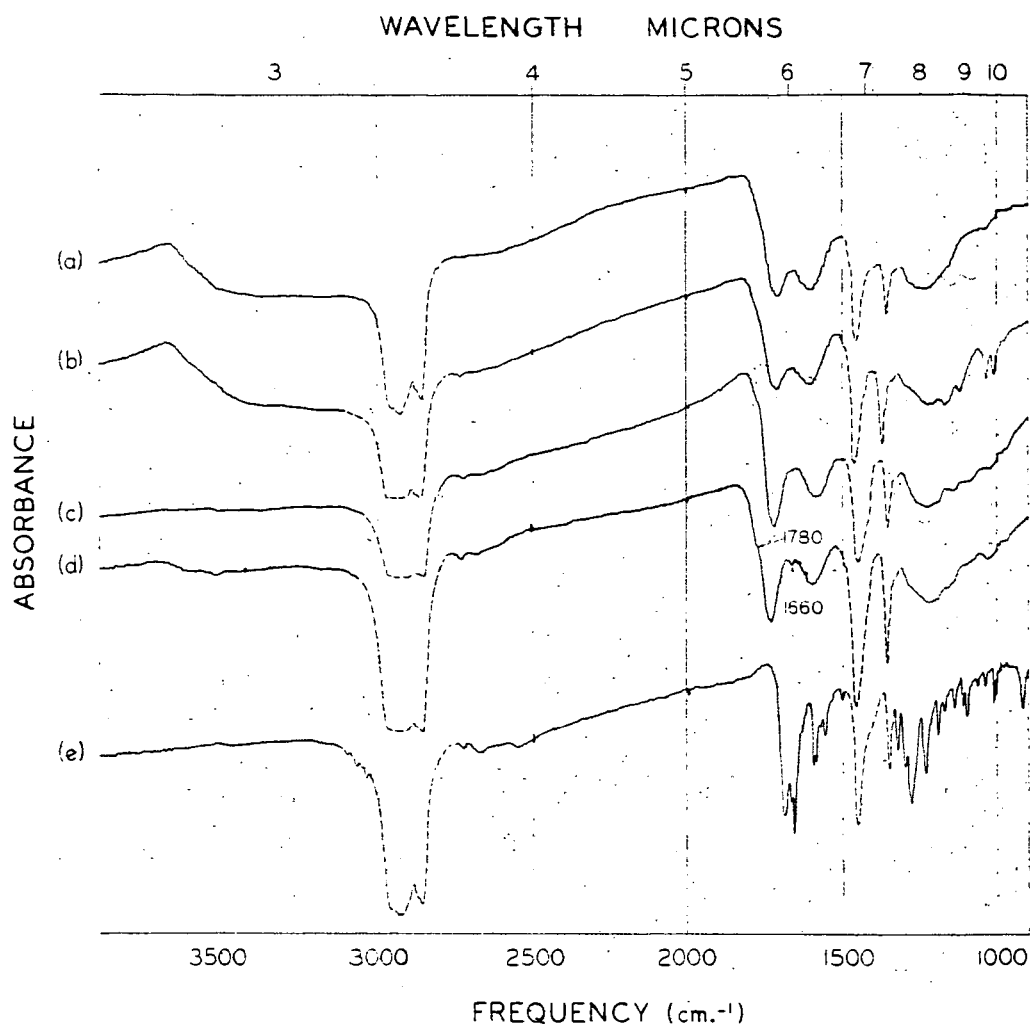


FIGURE 2. Humic acids and derivatives.

- (a) parent humic acids.
- (b) treated with diazotized sulfanilic acid.
- (c) methylated.
- (d) product of (c) treated with acetic anhydride.
- (e) 2-(p-carboxylphenyl)-1,4-naphthoquinone.

HUMIC ACIDS FROM LEONARDITE -- A SOIL CONDITIONER AND ORGANIC FERTILIZER

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The term "humic acid" was first applied in 1826 by Sprengel (9) to that brown amorphous precipitate which is obtained by acidifying the alkali extract of decayed organic matter in soil. Since the inception of the term, humic acids have been extracted not only from soil but also from peat, brown coal, oxidized bituminous coal, and even from artificial materials obtained in the laboratory by action of inorganic acids or oxidizing agents on carbohydrates, proteins, and phenols. Odin (8) in 1922 redefined humic acids as yellow-brown to black-brown substances of unknown constitution, formed in nature by decomposition of organic materials under atmospheric influence or in the laboratory by chemical action. Humic acids can split off hydrogen ions and form typical salts with strong bases and usually are insoluble in water, soluble in alkali, and reprecipitated by acid. In general, humic acids are not chemically uniform substances, but are hydrophilic, reversible colloids with molecular weights varying from 300 to as high as 10,000 units. Their micelles carry a negative charge. The alkali solubility of humic acid is due to carboxyl and phenolic hydroxyl groups which account for about 22 percent of the weight of the molecule.

Humic acid is an essential part of soil. It is this material, present in good soil, that fixes nitrogen, makes available to the plant, through base exchange, the soil nutrients, and improves the physical structure of the soil. In recent years, much research has been conducted, particularly in India, Japan, Germany, Russia, and France, on replenishing the depleted humic acids of soils with the so-called "regenerated humic acids" obtained by oxidation of coal. These regenerated acids, which closely resemble the natural humic acids, have either been added directly to the soil or first supplemented with plant nutrients. Greenhouse and field tests have shown that these humic acid preparations improve plant yields (3), decrease loss of moisture from the soil (6), and increase the workability of the soil (2).

As a convenient and commercial source of humic acids, extensive reserves of naturally-oxidized lignite occur with virtually all lignite outcrops in North Dakota. This naturally-oxidized material, which contains up to 86 percent humic acids on a moisture-and-ash-free basis, has been given the name "leonardite," after A. G. Leonard, first director of the North Dakota Geological Survey, who did much of the early studies on these deposits (1). Leonardite is a coallike substance similar in structure to lignite, but significantly different in its oxygen and ash contents. In Table 1 the ultimate analyses of lignite, leonardite, lignite oxidized with air in the laboratory at 150° C, and humic acid extracted from leonardite with 1N NaOH are compared. The ash content of leonardite varies from mine to mine but is usually between 15 and 30 percent on a moisture-free basis.

TABLE 1. - Analyses of lignitic materials, percent

	Leonardite	Lignite	Oxidized lignite	Humic acid extracted from leonardite by 1N NaOH
Ash (mf)	18.7	10.0	10.7	3.9
Hydrogen (maf)	4.0	5.1	2.9	3.4
Carbon (maf)	65.2	72.8	65.4	63.5
Nitrogen (maf)	1.3	1.2	1.4	1.3
Oxygen (maf)	26.6	19.9	29.2	31.1
Sulfur (maf)	2.9	1.0	1.1	0.7

AMMONIATION OF LEONARDITE

Nitrogen-enriched coal humic fertilizers have received much emphasis in the past few years. Recent investigations have indicated that these products perform well as conventional fertilizers and release nitrogen more slowly. The main problem in technology is to develop a product with sufficiently-high nitrogen content (around 20 pct) which will still remain commercially competitive.

To determine if leonardite could be ammoniated to a product containing sufficient nitrogen for use as an organic fertilizer, samples were prepared by three different methods: (1) Ammoniation in an aqueous slurry, (2) ammoniation in an upward moving gas stream through a column of dried leonardite, and (3) ammoniation under pressure of 2,000 psig at 200° C. The nitrogen analyses of these variously ammoniated leonardite samples and the analysis of an aqueously ammoniated humic acid extracted from leonardite appear in table 2. The increase of nitrogen content of leonardite, even under radical conditions, is not sufficient for it to be used as an organic fertilizer. The nitrogen content of the ammoniated humic acid increased 2.5 times over that of the correspondingly ammoniated leonardite sample. The higher ash content, as well as the 15-percent nonhumic carbonaceous material in the leonardite, accounts for the decreased reactivity with ammonia. Therefore, to prepare a high-nitrogen organic fertilizer, the humic acids would first have to be extracted from the leonardite.

TABLE 2. - Nitrogen analyses of variously ammoniated samples, percent
(Moisture-free basis)

Sample	Method of ammoniation		
	1	2	3
Leonardite	3.87	2.82	11.15
Humic acid	8.13	-	-

RECOVERY OF HUMIC ACIDS FROM LEONARDITE

One part of the work at this laboratory was to find an inexpensive, rapid method for obtaining from leonardite bulk quantities of low-ash humic acids which could be used in preparing a soil conditioner and high-nitrogen-content organic fertilizer. The humic acids in leonardite are bound to the ash largely as insoluble calcium salts. Therefore, to recover the humic acids requires not only a physical means

of removing the clay and sand, but also a chemical treatment to displace the calcium ion. In the past, alkali extraction of the humic acids with removal of the insolubles by centrifuging the humate solution was the standard procedure for obtaining low-ash humic acids (5). The alkali extraction process, however, requires not only fresh alkali for each lot of humic acid prepared but also an equivalent amount of acid to set the humic acid free, both of which are used up in the process. The large volumes of water, which must be used to obtain a low-ash product, plus the unfilterable nature of the alkali humate solution and acid-precipitated humic acid, make the alkali extraction of humic acids unattractive. The problem of eliminating alkali extraction as the method of preparing low-ash humic acids was approached by two different routes: (1) Removing the ash physically and chemically from the leonardite, leaving a carbonaceous product containing around 85 percent humic acid, and (2) extracting the humic acid from the leonardite with an organic solvent that could be reclaimed for further extractions.

Float-Sink Process. Figure 1 schematically represents the process that was used in our experiments. Partially-dried, pulverized leonardite was added to a separatory funnel containing CCl_4 as the dense medium. The float fraction containing the humic acids was transferred to a filter, and the CCl_4 was removed. The product was washed first with a dilute H_2SO_4 solution, then with warm water. The results of this experiment appear in table 3. A ZnCl_2 solution was tried in place of CCl_4 , but absorption of the solution on the carbonaceous material caused the latter to sink, resulting in a low yield of humic material.

TABLE 3. - An examination of the float-sink process, moisture-free basis, results given in percent

<u>Feed</u> <u>Ash</u>	<u>Product</u>		<u>Tailings</u>	
	<u>Yield</u>	<u>Ash</u>	<u>Humic Acid</u>	<u>Yield</u> <u>Ash</u>
17.7	73.1	3.5	89.0	17.4 56.8

Note - Not included in data is loss of water-soluble material.

Flotation Process. The flotation process for ash separation is schematically depicted in figure 2. The as-received, pulverized leonardite was added to the flotation cell, which contained a lignite-tar creosote fraction as a frothing agent. The froth was collected on a filter, and the filter cake was washed with dilute H_2SO_4 , followed by warm water. Results of a typical experiment in this process appear in table 4.

TABLE 4. - Analysis of the flotation process, percent

<u>Feed</u>		<u>Product</u>		
<u>Moisture</u>	<u>Ash (mf)</u>	<u>Moisture</u>	<u>Ash (mf)</u>	<u>Yield (mf)</u>
9.5	18.2	6.0	11.3	13.6

Organic-Solvent Extraction Process. The use of an organic solvent for extraction of humic acids would be most attractive if the solvent could be reclaimed by distillation and reused without reaction with or being absorbed on the humic acids. Polansky and Kinney (7) made an extensive survey of organic solvents and solvent mixtures regarding their ability to disperse humic acids from nitric acid-oxidized bituminous coal. They concluded that the most economical and most easily handled solvent for the commercial extraction of humic acids is a mixture of

acetone and water. Fowkes and Frost (4) showed that an acetone-water solution would extract humic acids from leonardite provided the leonardite was pretreated with dilute mineral acid. The amount of humic acids extractable was directly proportional to the amount of mineral acid used in the pretreatment. The several preliminary experiments conducted revealed that the most efficient extraction was accomplished using one liter of 80-20 acetone-water (percent by volume) and 10 grams of HCl (basis: hydrogen chloride) per 100 grams of leonardite (moisture-free). Ten grams of HCl per 100 grams of leonardite is slightly in excess of the acid that will be necessary to replace the calcium ion with hydrogen ions in an average leonardite sample. Sulfuric acid was tried in place of HCl as the source for the displacing H-ions, but the resulting CaSO_4 , mixed with the humic acids, resulted in an unfilterable product with a high ash content. In the first experiments, the mode of extraction was a countercurrent column. An acetone-water-HCl pretreated leonardite slurry was added to the top of the column while a solution of acetone-water was forced slowly upward through the slurry. The yields of humic acids were good, but the ash content of the product was high, indicating some carryover of ash. Later experiments showed that sedimentation of ash and nonhumic carbonaceous material in an acetone-water-HCl solution is quite rapid; thus a simple settling tank replaced the countercurrent column in the process. A flow diagram of the process appears in figure 3. The results of the experiments appear in table 5.

TABLE 5. - Analysis of the acetone-water-HCl extraction of humic acid from leonardite, moisture-free basis, percent

Feed Ash (mf)	Product			Tailings	
	Yield (mf)	ash (mf)	NaOH-soluble (mf)	Yield (mf)	Ash (mf)
17.8	64.9	1.8	96.8	31.1	38.2
		Elemental (maf)	C 63.5		
			H 3.8		
			N 1.0		
			S 0.7		
			O 31.0		

Note - Not included in data is loss of water- and acid-soluble material

DISCUSSION

A comparison of the three processes investigated reveals the drawbacks of the float-sink and the flotation processes. The float-sink separation requires a non-polar medium, carbon tetrachloride, which is absorbed to some extent on the leonardite. The use of CCl_4 , plus the fact that the leonardite must be partially dried before separation, makes this process unattractive commercially. The flotation process did not produce the desired results. Owing to the low hydrophobicity of leonardite, caused by the large number of carboxyl and hydroxyl groups on the micelle's periphery, the yields of humic acids were low and their ash contents high. Attempts to precondition the leonardite with a light neutral fraction of coal tar to increase its hydrophobicity failed. Changing the frothing agents several times also gave poor results. The acetone-water-HCl extraction of humic acids lends itself most favorably to a commercial process. The yield of low-ash product is high. The acetone is easily recovered by distillation at a low temperature, and the loss is very small. Acetone does not react with, nor is it absorbed on, the humic acids. The process requires

simple equipment (a sedimentation setup works quite well), and the insolubles settle rapidly. The humic acids are easily filtered once the acetone is removed, and a minimum amount of wash water is needed to obtain a low-ash product.

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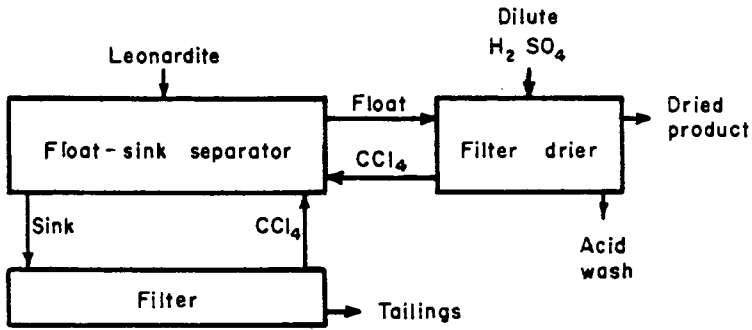


Fig. 1 Float-sink separation.

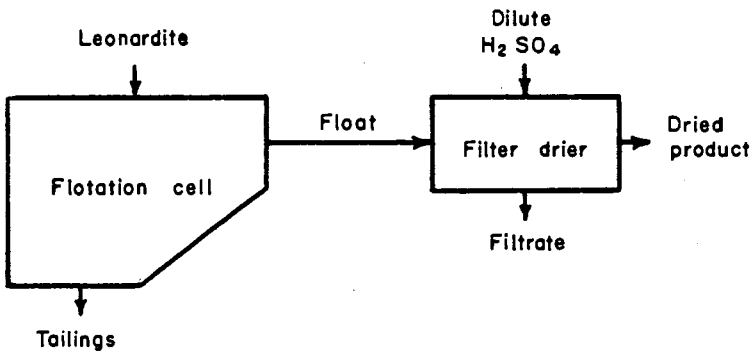


Fig. 2 Flotation process.

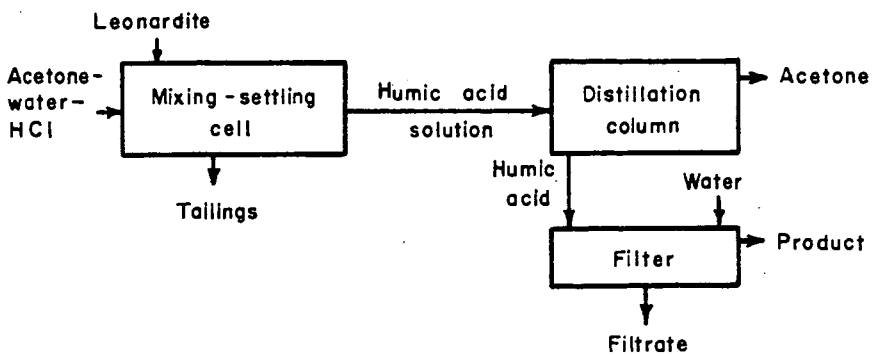


Fig. 3 Organic-solvent extraction.

HUMIC ACIDS FROM SUBBITUMINOUS COAL - A STUDY OF CONTROLLED DRY OXIDATION

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During the past few years, advances in humic acid chemistry have made it increasingly clear that humic acids offer an interesting and fairly direct route to large-scale chemical utilization of coal, and several commercial products containing (or derived from) them are, in fact, already being marketed (1,2,3). Despite this progress, however, processes by which humic acids form from and in coal are, like their detailed structure, still only incompletely understood and merit further investigation.

By definition, humic acids are brownish-black, alkali-soluble solids which can either be recovered from naturally weathered coals (4,5) or, alternatively, be prepared by controlled oxidation. The latter procedure, which is in principle to be preferred to reliance on necessarily random and somewhat uncertain natural processes, may take two basic forms. Pulverized coal can either be heated and reacted with air or oxygen (or with an oxygen-enriched air stream), in fluidized or static bed (6,7,8,9,10); or the coal may be suspended, conventionally, in hot aqueous alkali and treated under pressure (11,12,13) with air or oxygen. The choice between these techniques appears, at this time, to be largely a matter of personal preference since each has distinct advantages and disadvantages. For example, while wet oxidation will generally entail a substantially shorter reaction period than the dry process, its greater severity will usually mean lower yields of humic acids (and a proportionately greater concentration of low molecular weight, water soluble, degradation products in the final product mixture)(11).

Regarding the formation of secondary degradation products as basically undesirable, the Research Council of Alberta concentrated an initial study of the mechanism of the coal \rightarrow humic acid conversion on dry oxidation. This paper reports the behaviour of a typical Alberta subbituminous coal in such a process.

Experimental Procedure

In order to permit meaningful measurements which could be related to the ambient conditions under which oxidation was carried out, an apparatus of the form illustrated in Figures 1 and 2 was used. This afforded a gas-tight, closed circuit with provisions for pressure regulation, gas sampling and withdrawal of coal aliquots without interruption of the conversion process. As indicated in the diagrams, the total volume of the apparatus was approximately 2,200 cc.

Oxidation of the coal was achieved by means of dry oxygen which was introduced into the apparatus at the same rate at which it was consumed and which was thus maintained at a constant pre-selected pressure throughout each experiment. By arranging one-half of the constant-head oxygen supply bottle as a calibrated cylinder, accurate measurements of O_2 -consumption rates were possible. The total pressure was maintained at 1 atmosphere.

Instantaneous oxygen concentrations within the apparatus were continuously recorded on a Beckman F3 oxygen analyzer.

At the commencement of a run, the oxygen bottle was filled and the measuring cylinder completely topped with water. 15.00 gm of coal (-65 + 150 mesh Tyler), vacuum dried at 50°C were then charged into the fluidizer, the CO_2 and H_2O absorbers weighed (to the nearest 0.01 gm) and the fluidizer brought to the selected reaction temperature.

During the first 30 minutes after attainment of the reaction temperature, the rate of oxygen consumption would occasionally exceed the capacity of the supply valve, and in such cases, oxygen was furnished from a secondary source. By this means, it was possible to maintain the oxygen content uniform within $\pm 1\%$.

As the run progressed, 1 cc gas samples were withdrawn from time to time and submitted to gas-chromatographic determination of oxygen (as a check on the performance of the Beckman analyzer), nitrogen (as a test for leaks) and carbon monoxide. At regular intervals, 0.1 - 0.2 gm coal samples were also withdrawn for infrared spectroscopy, elemental analysis and functional group determination.

Measurements of alkali-solubles in these coal samples — conventionally accepted as a measure of humic acid content — were made by Kreulen's method and expressed as percentage humic acids in the sample (14). A minor modification in Kreulen's method was however, introduced in order to secure greater precision. Since the results obtained are distinctly time-dependent (cf. Figure 3) — presumably because of further oxidation in aqueous alkali — and since this drift could not be eliminated by blanketing with N_2 , humic acid contents were determined at 2 and 24 hours after initial suspension in alkali and extrapolated to zero time. Since the titre increased linearly with time for at least the first 30 hours after extraction, this procedure was considered justified and relatively error-free.

Results

Experiments so far have been limited to a single subbituminous coal with C \sim 71%, H \sim 4.2%. Results obtained are exemplified by Figure 4 which reproduces data gathered during a single experiment in which the oxygen concentration and temperature were held constant at 22.5% and 250°C, respectively. It will be observed that the carbon and hydrogen contents of the solid move asymptotically towards limiting values, while carboxylic acid concentration and total acidity (total acidity = carboxyl + phenolic OH) pass through a definite, broad maximum. The humic acid concentration likewise passes through a maximum. CO (not shown in Figure 4) appeared in the early stages of conversion, reached a maximum at 10 hours (5-15% by volume of gas) and disappeared completely beyond 65 hours. The significance of this observation is at this time unknown.

Material balances, which were established in all runs, checked within 5%. Experimental conditions could be duplicated to within $\pm 1\%$ in oxygen concentration and $\pm 2^\circ\text{C}$ in temperature, and the various measured quantities as shown in Figure 4 agreed to within $\pm 5\%$.

Figure 5 represents a repeat of the experiment illustrated in Figure 4, but this time extended to 450 hours. No measurements were made before 150 hours had lapsed. Beyond the first 150 hours, only insignificant changes appear to take place in the composition of the solid, but as shown by the continuous oxygen consumption, there is a steady loss of coal and already formed humic acid to carbon dioxide and water. At the conclusion of the test, only 46% of the original charge was recovered as compared with 66% in the test stopped at 150 hours.

Similar experiments were carried out at temperatures between 150 and 300°C, and at oxygen concentrations between 10 and 100%. Figure 6 illustrates the relation between temperature and functional groups at constant oxygen concentration. The same relationship was found in tests where the oxygen concentration was varied.

A summary of 20 experiments so far concluded in the study here under review is contained in Figure 7 a and b. For the particular coal examined in these runs, the pattern shows optimum humic acid conversion and recovery after 65 hours at 250°C and 25% oxygen concentration.

The humic acid content in the oxidized coal ran to ca. 95% and some 75% total solids (based on the initial charge) were recovered. The total (phenolic -OH plus -COOH) functional group concentration in the humic acid formed under these conditions runs to 10 milliequivalents/gm. The limiting C-H values are 61% and 1.8% respectively.

Discussion

Whether another coal would significantly alter the general pattern of results shown in Figure 7a and b, or whether it would only change the position of the maxima remains to be determined. Nor can anything, at this time, be said about possible catalytic effects of coal ash on the conversion process. Despite these limitations, however, the data so far at hand provide worthwhile new information.

As might be expected, variations in oxygen concentration and temperature tended to work in the same direction. Below 10% oxygen or 150° C, no significant reaction was observed. Above 80% oxygen or 300° C, rapid and complete oxidation of the coal to CO₂ and H₂O was found. For any conditions within this general range the carboxylic acid content rose through a maximum and then decreased (although the measurements were not always continued into the fall-off region). The total acidity likewise passed through a broad, but less pronounced maximum. These maxima occurred at shorter times as oxygen concentrations or temperatures increased.

The results illustrated in Figure 6 show that a temperature variation markedly influences the carboxyl concentration, which may range from 1 - 9 m.eq./gm. On the other hand, the total acidity is much less temperature dependent. Production of a humic acid principally characterized by either -OH or -COOH contents is, accordingly, dependent upon a more careful choice of experimental conditions than would be required if a predetermined total acidity only is to be afforded.

Since other results — though as yet incomplete — indicate that oxygen concentration has the same effect as temperature on the content and composition of the functional groups, the same statement may apply to this variable.

Another finding relates to the infrared spectra of partially reacted coal samples. These spectra, which were measured in order to gain information about reaction products not encompassed by other methods employed, did in some (but not all) series show pronounced absorption bands at 1850 and 1785 cm⁻¹ and thereby indicate the existence of 5-membered ring cyclic anhydrides (15, 16). To our knowledge, such components have not previously been reported from studies of the coal → humic acid conversion and now raise the question of whether they are intermediates in the reaction sequence leading to humic acids or merely the result of dehydration of already formed humic acids. Because the answer to this question would provide experimental evidence for or against Tronov's postulates (17), suggesting that such cyclic anhydrides might be essential steps in the mechanism of conversion, a study pertaining to this problem is currently in progress in these laboratories.

Finally, some significance may be attached to the variations of carbon and hydrogen contents (cf. Figure 7a). The approach of these quantities to limiting values which cannot, apparently, be lowered by extending the reaction period, lends interesting experimental support to Francis' work on "oxidation tracks" and tends to validate the "limiting oxidation line" of his diagram (18). Prolonged oxidation, increased reaction temperatures, and/or higher oxygen concentrations appear to accomplish little more than conversion of carbon and hydrogen to CO_2 and H_2O respectively.

In the light of Figure 7a and b, it is obvious that optimum conditions for oxidation of a given coal, and for the production of a humic acid possessing predetermined properties, can be chosen with some ease. It is, however, equally obvious that artificial production of humic acids is subject to several limitations which arise as much from the meta-stability of humic acids as from the relatively low reaction rates. If it is accepted that humic acids hold an industrially important potential, further studies of their formation from coal are therefore imperative.

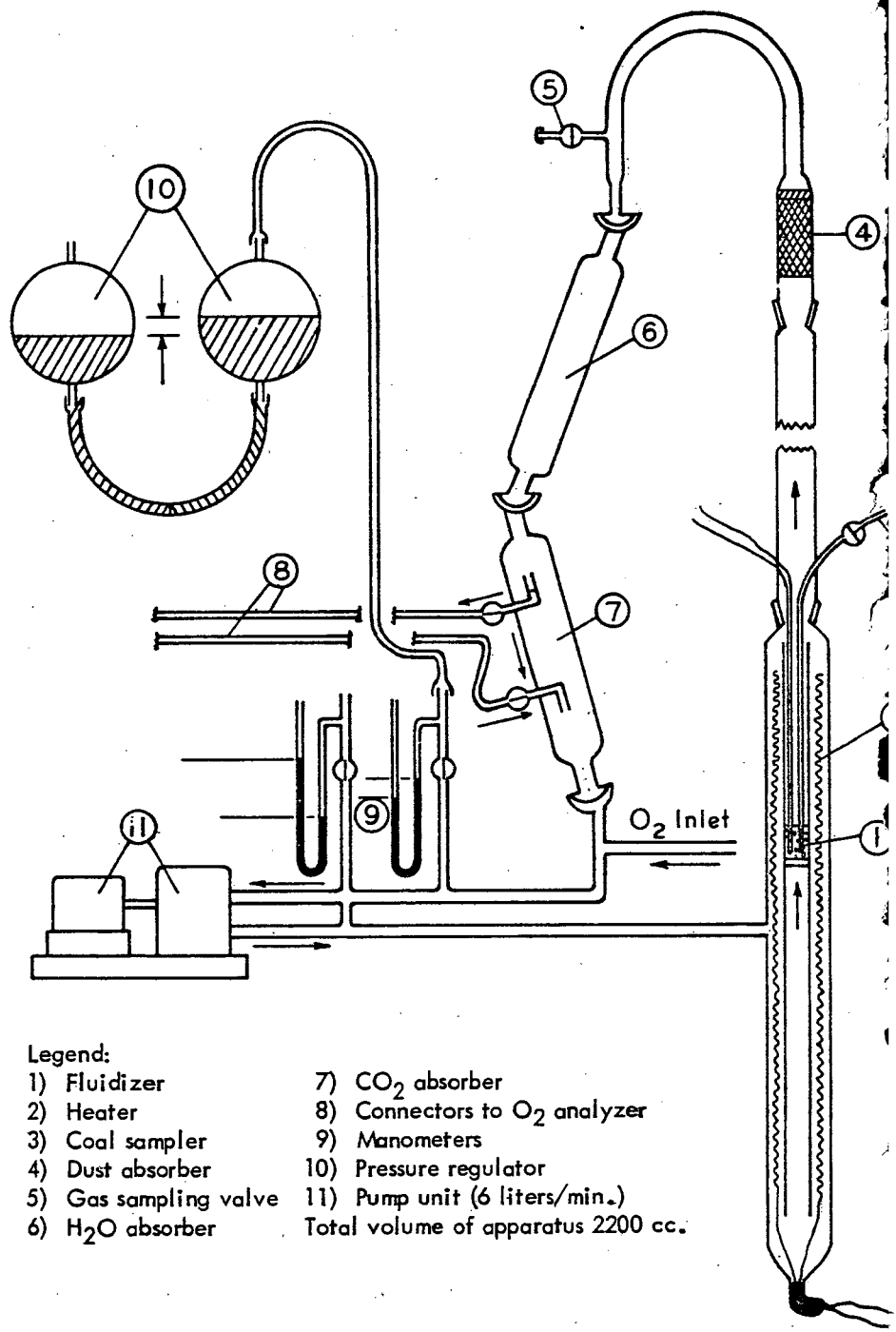
Acknowledgements

We are indebted to Dr. J. C. Wood for assistance in various phases of the experimental work (and particularly for his help in interpreting the infrared spectra) and also wish to thank Mr. J. F. Fryer for the analytical data and Mr. E. Kyto for help and inventiveness during the design and construction of the apparatus.

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FIGURE 1



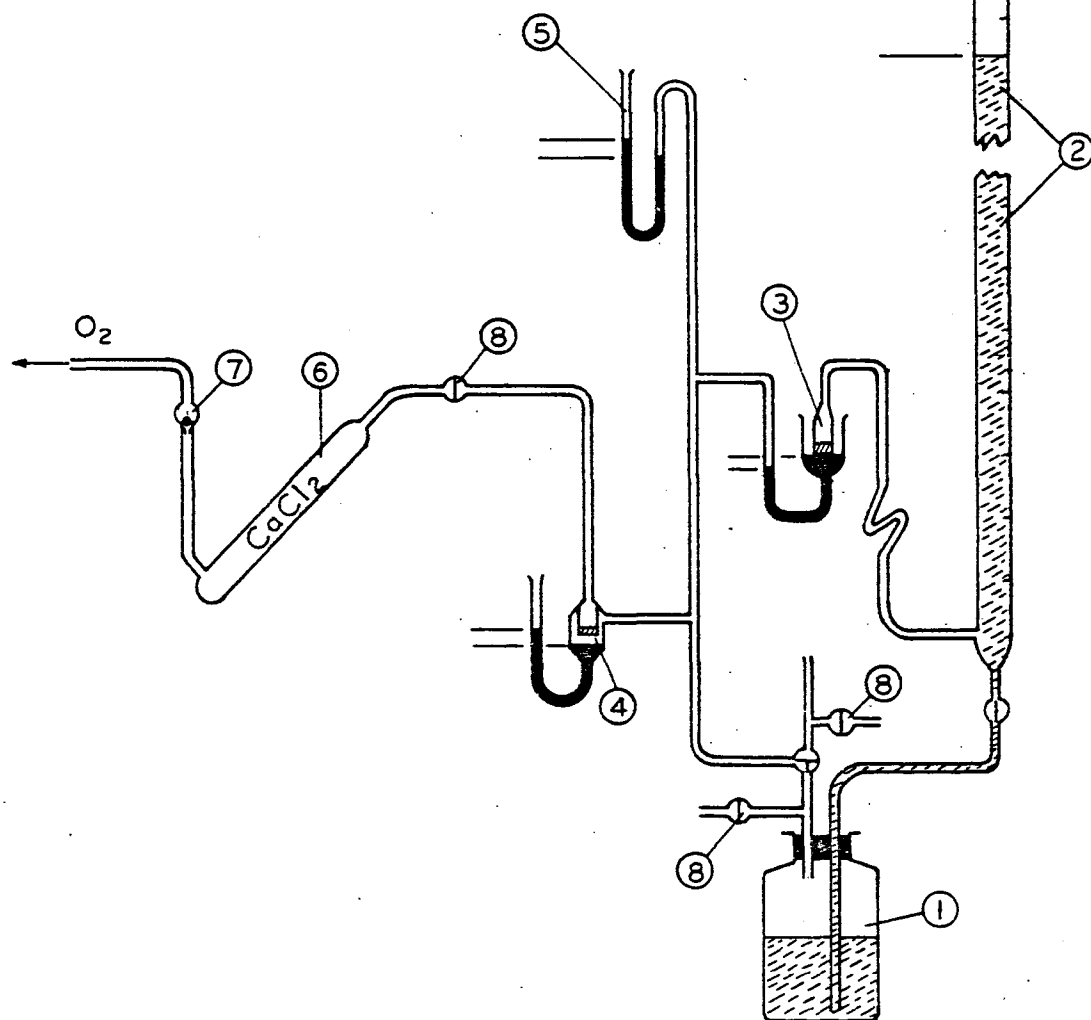
- Legend:
- | | |
|------------------------------|--|
| 1) Fluidizer | 7) CO ₂ absorber |
| 2) Heater | 8) Connectors to O ₂ analyzer |
| 3) Coal sampler | 9) Manometers |
| 4) Dust absorber | 10) Pressure regulator |
| 5) Gas sampling valve | 11) Pump unit (6 liters/min.) |
| 6) H ₂ O absorber | Total volume of apparatus 2200 cc. |

COAL OXIDATION APPARATUS
(not to scale)

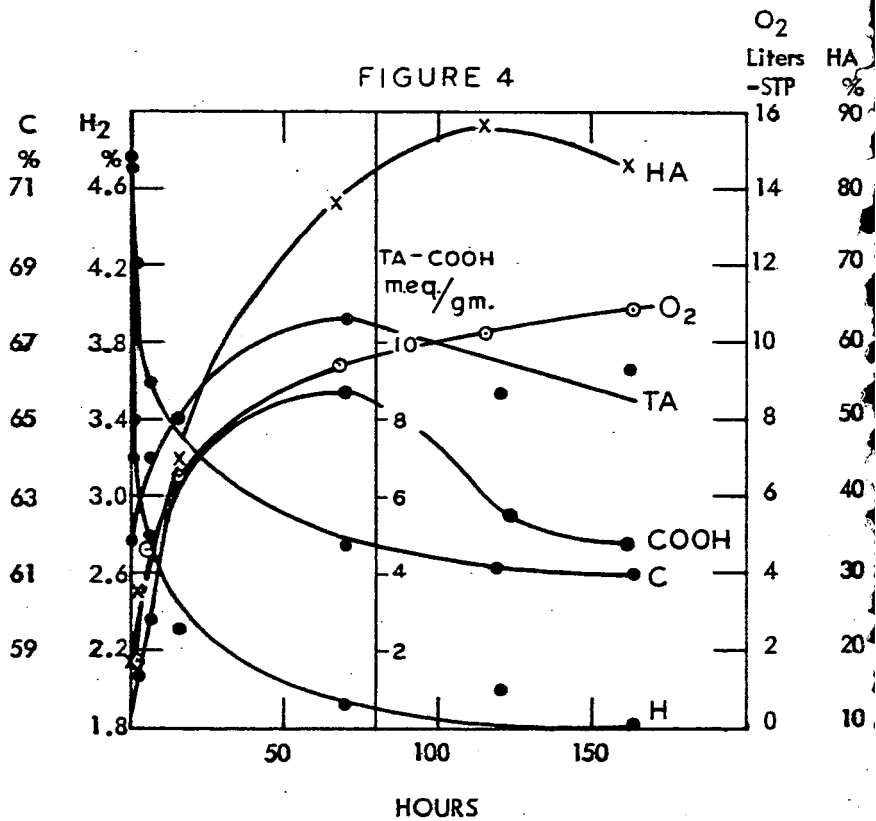
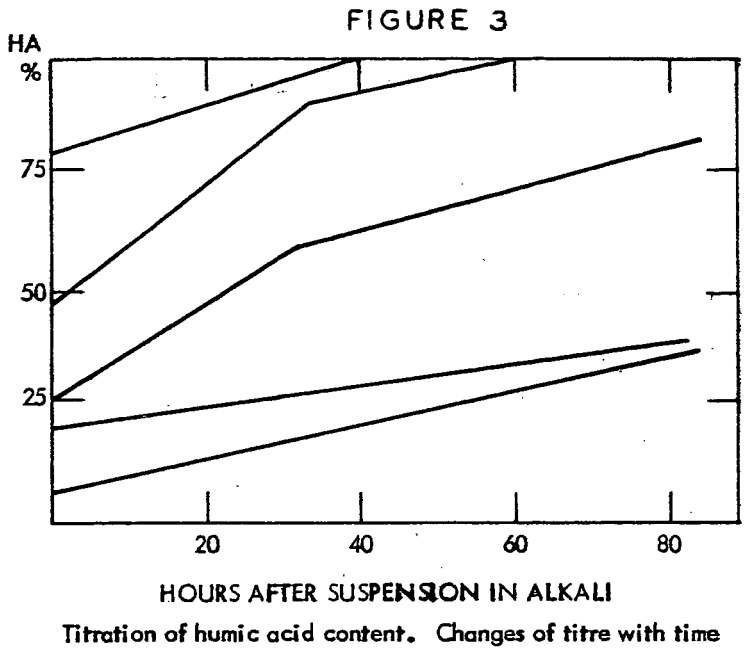
FIGURE 2

Legend:

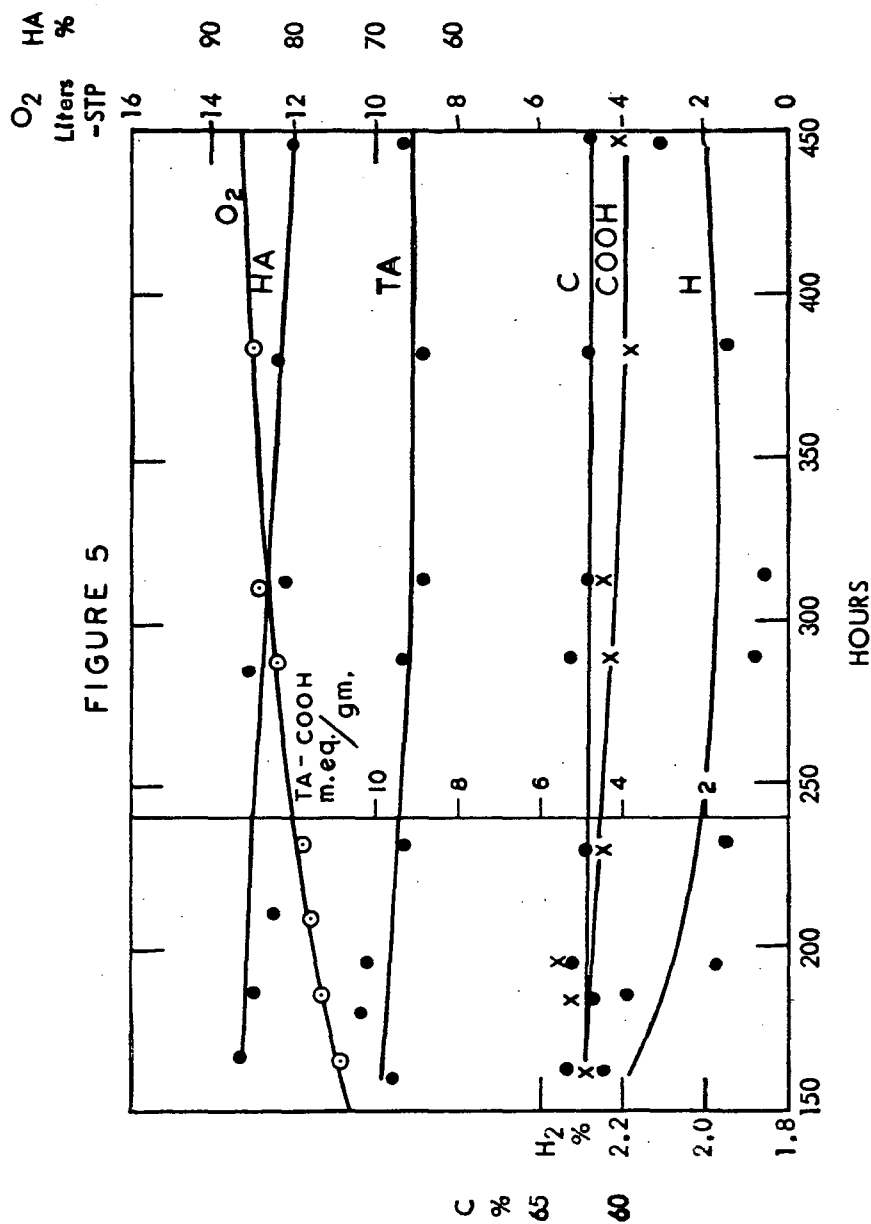
- 1) 4 liter O_2 - reservoir
- 2) 280 cm measuring column
- 3) Adjustable mercury-filter disc air trap for (2)
- 4) O_2 - trap
- 5) Manometer
- 6) H_2O absorber
- 7) Mercury bead capillary valve
- 8) Auxilliary valves



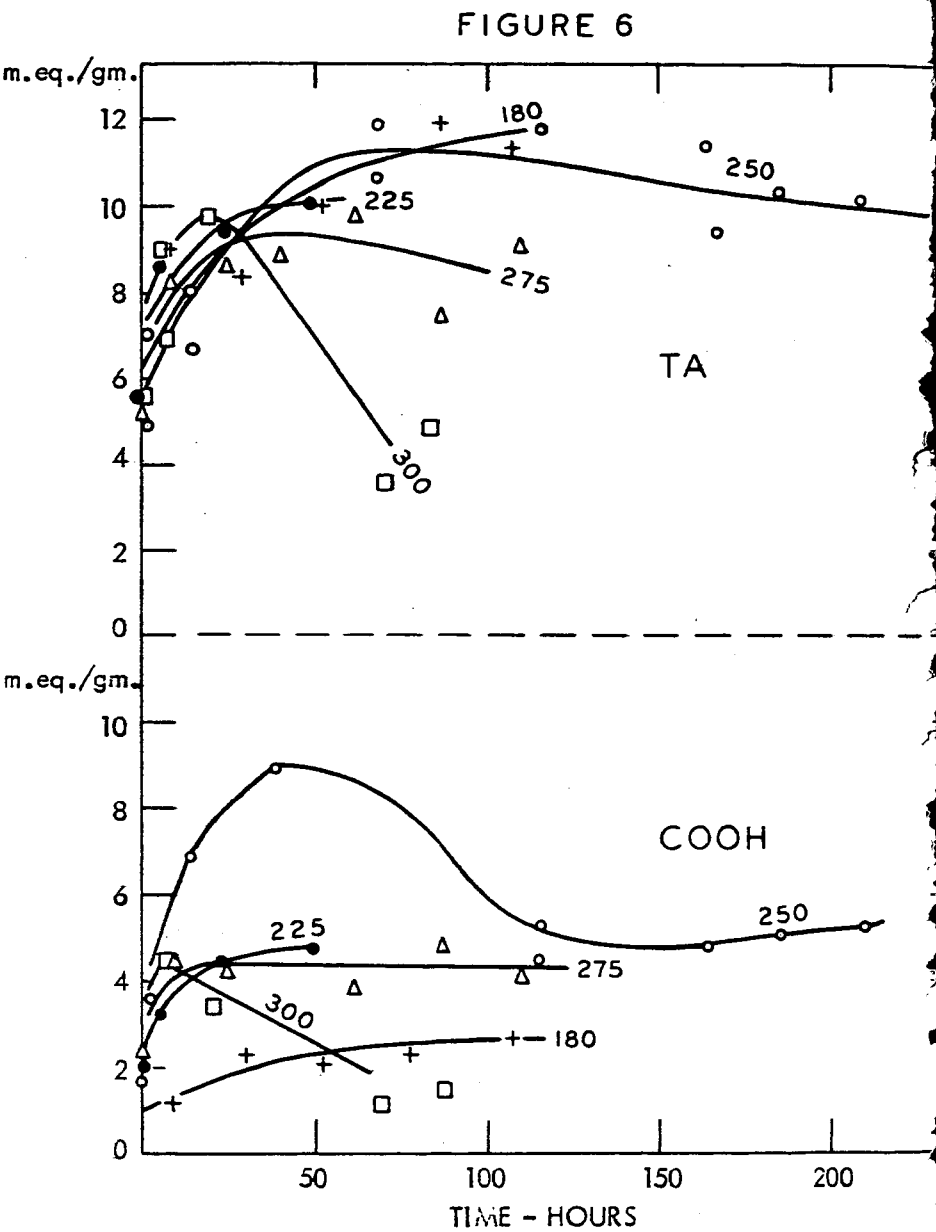
OXYGEN SUPPLY APPARATUS
(not to scale)



Variations of humic acid content and properties with time
Legend: HA = humic acid content in % of sample, TA = total acidity, COOH = carboxyl, C = carbon, H = hydrogen, O₂ = oxygen consumption

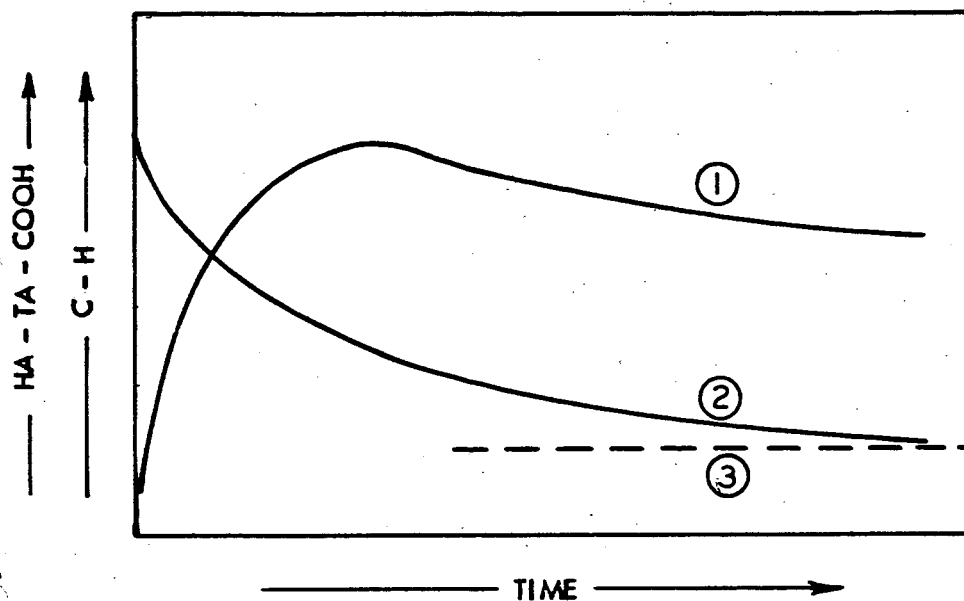


Variations in humic acid content and properties with time. Legend as in Figure 4



Variations in functional group content with temperature

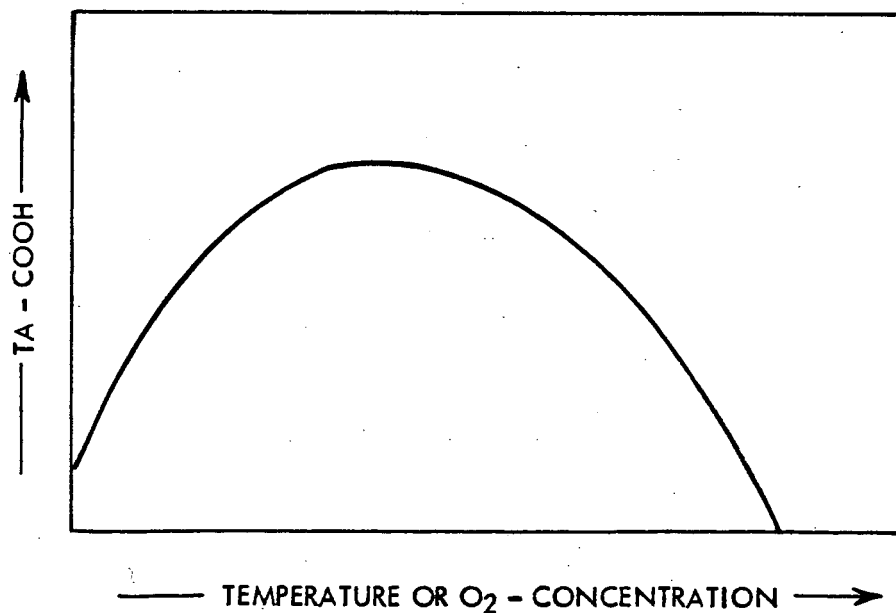
FIGURE 7a



Variations of humic acid content and properties with time.

1) HA - COOH - TA 2) C - H 3) C - H limits

FIGURE 7b



Variations in functional groups with temperature or O₂ - concentration

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Peat can roughly be defined as the product resulting from a special arrested decay of dead vegetation. The more typical pattern followed by dead plants is to undergo complete decay, with conversion of the organic matter into gases that are released into the atmosphere, while the inorganic matter remains in the soil. This complex process can take place only when the characteristic needs of the microorganisms that bring it about are met; these include, among others, air, water, and suitable nutrients. When dead plants accumulate under water, however, air is excluded and only a partial decay takes place, together with physical disintegration. After some hundreds of millions of years the successive products are lignite, then bituminous coal, and ultimately anthracite coal. But at a relatively very early stage, after some 10,000 to 20,000 years, the product of this arrested decay is peat. Peat, then, represents the bare beginning of the coalification process.

Considerable data have been published on the areas of peat bogs in various parts of the world, and on the amounts of peat in these bogs. It is probably safe to accept these data so far as they indicate orders of magnitude. Beyond this, they must be treated with considerable reserve, for the very good reason that virtually nowhere has the utilization of peat been great enough to justify the tremendous expense of an exhaustive accurate survey. (Two exceptions to this statement may be noted: first, in the Soviet Union and in Ireland, where there are large fuel peat industries; second, in any other area where there might be an exhaustive local survey for a specialty high-value peat, such as horticultural-grade sphagnum.) With these disclaimers, the following estimates are probably as good as any:

Table 1

World Peat Deposits¹

<u>Country</u>	<u>Square Miles</u>	<u>Country</u>	<u>Square Miles</u>
U.S.S.R.	65,000	Great Britain	9,400
Canada	37,000	Ireland	4,700
Finland	30,000	Newfoundland	3,000
Sweden	19,000	Norway	2,900
U.S.A.	11,200	Austria	1,500
Germany	9,900	Denmark	400

In addition, peat deposits are known to exist in the other continents, but there we cannot make even uneducated guesses.

Data on the amount of peat in the bogs are even less reliable than the bog areas, since the depths of peat deposits will vary over wide ranges; typically, from 4 to 20 feet within a given bog, and depths as shallow as

Page 2

a foot or two, and as deep as 50 feet or more, are not unknown. The following estimate, that of Kazakov,² again is presented only as an order of magnitude:

Table 2
World Peat Reserves²

	Billions of Tons ^a
U.S.S.R.	153
Rest of world	
Europe (except U.S.S.R.)	24.8
North America	18.1
All others	27.1
	<u>70</u>
World total	223
(a) On an air-dried (30% moisture) basis	

And for the United States, we have the data of Soper and Osborn:³

Table 3
United States Peat Reserves³

State	Peat Area, millions of acres	Peat, millions of tons, air- dried basis
Minnesota	5.2	6,835
Wisconsin	1.0	2,500
Florida	—	2,000
Michigan	—	1,000
Virginia-North Carolina	—	700
New York	0.8	480
Maine	—	100
California	0.06	72
Ohio	0.05	50
All others	—	<u>90</u>
Total		13,827

Data on current production are presented in Table 4. The discrepancies between the sums of the values for individual countries and the totals at the bottom are due to the fact that the values in the table are based on data from two different sources,^{4,5} and some of the values are estimates by this author in an attempt to reconcile these sources. Only the larger producers are listed.

Table 4

World Peat Production in 1960

Country	Thousands of Tons		Sum
	Fuel	Nonfuel	
U.S.S.R.	59,100	86,000 (est.)	145,000 (est.)
Ireland	4,510	14	4,530
West Germany	871	895	1,780
East Germany	—	—	550
Netherlands	—	—	500
U.S.A.	none	471	471
Sweden	275	70	345
Norway	198	42	240
Denmark	—	—	187
Canada	negligible	185	185
Finland	132	6	138
Poland	—	—	125
Total (estimates) ^s	60,000	100,000	160,000

A few conclusions are immediately evident from these data. First, with some 90 per cent of world production, Russia is by an overwhelming margin the largest factor in the world peat industry. Second, only in Russia and in Ireland does power from peat make up a substantial fraction of the national energy supply. Third, since nearly all the "nonfuel" use is in agriculture, world consumption of peat in agriculture is apparently greater than the amount burned for fuel. ("Apparently" because Russian data on nonfuel utilization are much less complete and up-to-date than their fuel data, and were here estimated by extrapolation.) Finally, in this country peat utilization is synonymous with agricultural utilization. Before going into this, it might be useful to describe the various types of peat.

While peats are classified by soils scientists into some half-dozen or more well-defined groups, commercial statistics^s are generally based on the following three classes:

Moss peat, or sphagnum peat moss, is peat derived largely from sphagnum and hypnum mosses. This is a light-colored material, springy, with a well-defined layered structure in its natural state. It is the least decomposed of the peats, with the lowest bulk density (7-15 lb./cu. ft.), the lowest ash content (usually under 4 per cent), the lowest pH (typically 3.5 to 5.0), and the highest moisture-holding capacity—up to 20 times and more its own weight of water. Virtually all peat imported into the United

Page 4

States consists of sphagnum, which commands a much higher price than the other varieties.

Reed-sedge peats are peats derived from reeds, sedges, grasses, cat-tails, and various shrubs. They are much more decomposed and disintegrated than sphagnum peats, have a higher bulk density (20-35 lb./cu. ft.), are usually dark in color, and tend to have a fibrous structure that is due to their content of relatively undecomposed stems and roots. The pH range is 4.5 to 7.0; the ash content will typically vary from about 4 to 15 per cent but may be a good deal higher; and the moisture-holding capacity is about one-half that of sphagnum. About one-half to two-thirds of the peat produced in this country is reed-sedge.

Humus is a catch-all name for peats so completely decomposed and/or disintegrated as to have lost their biological identity. Humus may be native peat, or it may derive from peat land on which crops have been grown. The terms humus, muck, and peat soil tend to over-lap, but the ash content usually serves as a convenient if arbitrary dividing line between "true" peat—ash under 40 per cent—and peat soil—over 40 per cent. About one-third of United States domestic production can be classified as humus.

Although the nitrogen content of peat, some 1 to 3 per cent, is not negligible, this nitrogen is released so slowly that peat is not considered to have any particular value as a direct fertilizer. Its value in horticultural applications lies, rather, in its soil-improvement characteristics.^{7,8} The addition of peat to a heavy clay soil, for example, brings about a tremendous improvement in the structure of that soil. And the water-holding capacity of peat is beneficial to any soil, since peat tends to supply a buffer-type action: it will absorb excess moisture during periods of too-heavy rainfall, and release this water during drought periods, thus providing the growing plant with a more uniform supply of water. This is notably advantageous in sandy soils. These properties are particularly beneficial in the building of new lawns, for which large quantities of peat are mixed into the soil prior to the application of seed or sod. For similar reasons, peat is widely used as a mulching agent for ornamental plants and shrubs.

In addition to the major use just described for soil improvement, peat is used in a variety of other ways relating to agriculture. Potting soils, widely marketed in small plastic bags, are generally mixtures of peat and soil. Mushroom growers have been using peat for mushroom beds, and this practice appears to be growing.⁹ A relatively new outlet for peat is found in the small molded peat pots now sold in most garden supply stores. These were first developed in Norway, and substantial amounts of Norwegian pots are marketed in this country. More recently, several American producers have begun to manufacture these pots from domestic peats. And similar pots are now being made in Ireland on a different principle. Unlike

the Norwegian and American pots, which involve a high pressure molding operation, the Irish pot is made by cutting a suitable cavity in a block of air-dried peat. This preserves the original structure and porosity of the peat, and it is claimed that the greater cost of production is justified by the superiority of the product.

Another quite recent development shows particular promise. As the culmination of work extending over more than a decade, Baker¹⁰ and his colleagues developed the "U.C." formulas for nursery soil mixes, consisting essentially of mixtures of peat moss and fine sand to which suitable nutrients are added. This has attracted widespread and favorable interest. For example, the Irish national peat establishment, Bord na Mona,¹¹ has developed a modification of the U.C. formula adapted to European conditions, and is now marketing this material as the U.C.E.E. seed and potting compost.

Several older agricultural applications still account for substantial quantities of peat consumption. One of these is the use of peat for animal bedding and poultry litter. Its high moisture capacity makes the peat particularly suitable for this purpose, and the exhausted product consists of fine manure whose value is greatly enhanced by the soil-conditioning property of the peat with which it is combined. Another well-established utilization consists of the addition of 5 to 10 per cent peat to manufactured fertilizers. This is based on the fact that some of the components of commercial fertilizers are hygroscopic, so would become sticky in humid weather and hard-caked under dry conditions. By absorbing or releasing moisture as needed, the peat tends to keep the fertilizer free-flowing. Still another application of the moisture-holding property of peat is found in its use in the packaging of cut flowers and certain vegetables. Asparagus crates, for example, are sometimes lined with a layer of peat which is then wetted. By slowly releasing its moisture, the peat maintains the asparagus in good condition during shipment.

The one agricultural use which may ultimately have the greatest potential of all would be to incorporate into peat, by chemical or microbiological means, suitable plant nutrients in the right proportions and with the necessary characteristics of availability and rate of release, such as to add fertilizer properties to the soil-conditioning activity which peat already possesses. Needless to say, this problem has been and is being given energetic study in almost every laboratory where peat is looked at from a chemical or engineering point of view. Equally needless to say, the fact that a major industry of this nature does not exist indicates that the problem is still quite far from a solution. Nevertheless, two operations are in existence today in which such a peat-fertilizer-soil-conditioner is being produced. One is in Austria,^{12,13} where the Österreichische Stickstoffwerke A. G. produces two peat derivatives of this nature--Humon and Voll-Humon. Humon is made by the reaction of air-dried peat (40% moisture) with anhydrous

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ammonia in the presence of air, at atmospheric pressure. The ammonia is completely absorbed in one pass with virtually no loss. This process raises the nitrogen content from about 1 to 3 per cent. The important consideration is the rate of release of nitrogen—about one-half becoming available the first year and the remainder within two years. The nitrogen content of the product is deliberately kept down to 3 per cent in order that as much humic material per unit of nitrogen as possible be supplied to the plant. The essential difference between Humon and Voll-Humon ("Complete Humon") is that the latter contains, in addition to nitrogen, the nutrients potassium and phosphorus, together with certain trace elements. A major problem with Humon and Voll-Humon appears to be that the cost of production still makes these products too expensive for ordinary agricultural use and thus limits their market to horticultural applications. Nevertheless, about 10,000 tons per year were being produced in 1957.

A related process is the one developed by the French company, Societe de Produits Chimiques et Engrais d'Auby.^{12,13} The process involves a fermentation of peat following a treatment with ammonia and other chemicals. Here, too, the cost of the product appears to present the major obstacle to widespread utilization of the process. Annual production was said to have been about 100,000 tons before the Algerian war destroyed a major part of the market.

Before we turn to nonfuel uses other than agriculture, which are found only outside the United States, a few statistics on United States production and consumption may be in order.

Table 5
United States Peat Consumption¹⁴

	Total Consumption, Thousands of Tons	Domestic Production		Domes- tic Pro- ducers	Imports	
		Thou- sands of tons	Value, Thou- sands of Dollars		Thou- sands of tons	Value, Thou- sands of Dollars
1939	134	55	362	39	79	1,204
1946	225	141	1,006	59	84	2,704
1950	255	131	1,143	48	124	3,867
1955	503	274	2,283	82	229	9,262
1958	597	328	3,446	81	269	12,034
1959	706	419	4,372	105	287	13,580
1960	735	471	5,138	115	264	13,509
1961	777	525	4,991	123	252	13,178

A few trends become apparent from these statistics. First, the use

of peat has shown a steady increase in this country with no sign yet of levelling off. This is understandable—we have become a nation of homeowners, and every lawn and every garden represents a new market for peat. Second, while domestic production shows a steady increase paralleling consumption, imports seem to have reached a maximum and leveled off. What is really surprising is the dollar value of the domestic product compared with that of the imported. In 1961, for example, we find 525,000 tons of domestic valued at about 5 million dollars, for an average of slightly less than \$10 per ton, as compared with an average value of the imports of over \$50 per ton—5 times as great. Two factors are involved. In the first place, the domestic prices reflect the proceeds received by the original producer f.o.b. plant, and frequently are for a product shipped in bulk. The imported prices are those paid by the importer p.o.e., and invariably include the cost of a rather expensive package. Nevertheless, there remains a considerable spread, and this is due to the fact that nearly all the imported material is peat moss, which commands a much higher market price than reed-sedge and humus, of which most domestic production consists. In fact, the major reason that imports are so high is that only a very small proportion of American peat deposits are sphagnum moss of suitable size and quality for commercial operation.

The next table shows, for the year 1960, the major sources of the peat consumed in the United States and the major outlets. The discrepancy between supply and utilization is due to the fact that only the material sold in commercial channels is listed in the consumption, with no account taken of peat utilized in captive operations.

Table 6

Peat in the United States—1960¹⁴

<u>Major Domestic Sources</u>	<u>Thousands of Tons</u>
Michigan	214
Florida	39
California	33
Pennsylvania	31
Washington	28
Indiana	27
New Jersey	25
39 Other states	less than 10 each
<u>Major Foreign Sources</u>	
Canada	157
West Germany	84
Poland	8
Netherlands	8
Denmark	6

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Table 6 (continued)

<u>Major Uses</u>	<u>Thousands of Tons</u>
Soil Improvement	405
Potting Soils and Flower Packings	17
Miscellaneous	9

The nonfuel uses of peat outside of agriculture account for only a minor fraction of total peat consumption. On the other hand, one of them constitutes an important basic industry, and several show considerable interest and promise.

Perhaps the most important of these nonfuel nonagriculture applications of peat is its use as the raw material for the manufacture of activated carbon. The importance of activated carbon in sugar refining, gas purification, chemical processing, and other industries is well known. At least one of the major producers (Norit Co., Amsterdam)¹² makes most of its activated carbon from peat, and there are indications that others may follow suit. A serious limitation lies in the rather stringent specifications of the starting material. The nature of the (secret) process is such that the peat must be quite decomposed, to the extent that it sticks together like a damp mud when pressed by hand. At the same time, its ash content must not exceed about 3 per cent. So far as the writer knows, only one particular peat—a bog at the Holland-Germany border—has this combination of properties. The only low-ash American and Canadian peats are sphagnums, very little decomposed, and the ash content of the well-decomposed peats is rarely as low as even 6 per cent.

Since cellulosic substances constitute one of the major organic constituents of peat (15 to 50 per cent), the fermentation of peat to produce ethanol is a well-known process. However, it is not competitive with ethanol by other processes. On the other hand, the Russians^{12, 15} have developed a thermo-chemical processing of peat that at least in the Soviet economy is competitive. In this process the peat, only partially dried, is autoclaved with steam to destroy its colloidal structure. This makes it possible to dewater the peat by filtration, a process which the colloidal nature of untreated peat renders impossible. The process is therefore called "artificial dehydration." Some chemical products are produced during the autoclaving, and others during a subsequent fermentation, with the following overall yields from 1000 kg. of peat (37 per cent moisture basis): 6-8 liters of ethanol, 3.5-4 kg. of furfural and substituted furfurals, 700-750 kg. of peat fuel. Modifications under development would add 22-24 kg. of oxalic acid and 5-6 kg. of acetic acid to the above products. In 1957, a plant near Leningrad was operating at an annual peat consumption rate of 50,000 tons.

Processes for using peat for the manufacture of products such as wallboard, heat insulating plates, sound-proofing materials, and even papers and fabrics, are well known, and many patents have been issued. With suitable additives, these products can be made fire resistant. Before World War II the Soviets were known¹⁵ to produce heat insulating plates from peat on a large scale, but no current information is available. A related product from peat is a flooring material of rather high quality, which has been manufactured at various times in Sweden, Germany, and Russia, and probably elsewhere. And in the same category we find peat used as a filler in linoleum.

Wax constitutes another of the major organic constituents of peat (5 to 15 per cent), and the extraction of waxes from peat has been widely studied (Reilly, Ireland; Dragunov, Russia; Sundgren, Finland; Risi, Quebec). These waxes are comparable to the montan waxes from brown coal, and can be refined to a product comparable to Brazilian carnauba wax. But whether peat wax is competitive with these products remains to be seen.

A recent (1961) peat development that shows great promise is based on some work by the British Cast Iron Research Association,¹⁶ who found that the substitution of a particular type of peat for the coal dust or wood flour ordinarily used in iron foundry casting sands affords an improved product requiring less finishing. Current annual production of "Berkcoal," the trade name for peat meeting specifications for this purpose, is of the order of 12,000 tons.

Two minor uses of peat may deserve mention. During World War I, sphagnum moss was used on a large scale as a filler for surgical dressings and mattresses, an application based on its absorptive and antiseptic properties. And today in Germany, there are a large number of health spas whose major attraction consists of taking baths in a hot peat-water slurry. These are elaborate establishments, usually with one or even several physicians in full-time residence. The writer has no information as to how effective these peat baths are medically, but since the spa is usually located in beautiful mountain country far from the cares of everyday life, the overall effect is undoubtedly all to the good.

A final topic that should at least be mentioned is the use of peat lands for growing crops--either on native bogs, or on reclaimed peat land after removal of the peat. As an example of the first, suitably developed muck soils are highly regarded for crops such as celery and potatoes, while reclaimed bog lands are ideal for blueberries and cranberries. It should be emphasized, however, that the effective use of peat lands constitutes one of the major problems of soils scientists, particularly in the countries of Western Europe where arable land is scarce and precious, and that full realization of the potentialities of these lands still lies far in the future.

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MOLECULAR SIEVE PROPERTIES OF ACTIVATED ANTHRACITE

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Introduction

It is well known that coals exhibit molecular-sieve properties. Such properties are characterized by much higher $n\text{-C}_4\text{H}_{10}$ adsorption than $\text{iso-C}_4\text{H}_{10}$ adsorption at room temperature (1) and particularly by activated adsorption of N_2 and A at 77°K . (1, 2, 3, 4, 5). However, this molecular-sieve behavior in the case of raw coal is of little practical value, since the diffusion rate of the adsorbate into the pore system is usually very slow and the total adsorption capacity is usually very low.

There is an increasing interest and use, today, of molecular-sieve materials by the petroleum industry for the separation of straight from branched-chain hydrocarbons. Synthetic crystalline zeolites are being used almost exclusively for this purpose (6). Charcoals made from the pyrolysis of certain polymers show promise (7). In this paper, the possibilities of producing a suitable molecular-sieve material by the activation of anthracite is considered.

Experimental

Anthracite Used - A Pennsylvania anthracite, which was ground in a fluid energy mill to an average particle size of 6μ on a weight basis, was used in this study. The proximate analysis (air-dry basis) of the anthracite was: moisture, 1.2%; V. M., 8.2%; fixed C, 79.4%; and ash, 11.2%.

Devolatilization of the Anthracite - Prior to activation, the anthracite was devolatilized in a N_2 atmosphere at 950°C . for 6 hours. No attempt was made to analyze the product gases during devolatilization; but from previous studies on kinetics of volatile matter release from anthracite, most of the gas released was H_2 (8).

Activation of Anthracite - Because of the fine particle size of anthracite used, a down-flow fixed bed reactor was employed. The reactor, which was 2.25 in. i. d., 3.25 in. o. d., and 2 ft. long, was made of 10-18 steel tubing. The anthracite sample holder, which could be inserted into the reactor, was 304 stainless steel. Its dimensions were 1.87 in. i. d., 0.065 in. wall thickness, and 17 in. long. The bottom was perforated to allow for the passage of the gases. Gas mixing and preheater sections were present, before the reactor. The entire apparatus is described in detail elsewhere (9).

For a run, an oven dried sample of anthracite of known weight was placed in the sample holder. The sample was heated to activation temperature in N_2 and then reacted with a 90% CO_2 -10% CO gas mixture, at a total pressure of 1 atm. Following reaction, the sample was cooled in N_2 and the percentage burn-off measured from the loss in sample weight. Carbon monoxide was added to the inlet stream so that more uniform activation through the bed would occur. That is, it minimized the effect of small amounts of product CO strongly retarding the gasification reaction (10).

Apparatus to Measure Properties of Anthracite

Apparent density - The apparent density of the samples was determined by Hg displacement. A Hg porosimeter was used (11), in which the total pressure above the Hg was raised to 2,000 psi. At this pressure, Hg is forced into openings greater than ca. 1000 Å. Therefore, it is expected that the voids between anthracite particles were completely filled. At the same time, the volume of Hg forced into pores above 1000 Å. within the anthracite particles is thought to be negligible (12).

Helium density - Prior to the measurement, the samples were outgassed at 125°C. for 8 hours. The He densities were determined by the conventional method in which a measured quantity of He was expanded into a sample holder (held at 30°C.) of known volume containing a sample of known weight. A 30 min. period was found adequate to reach equilibrium.

Adsorption apparatus - A static adsorption apparatus of the typical design (13), containing Hg float valves, was used. All adsorption studies were conducted at $30 \pm 0.1^\circ\text{C}$. Prior to measuring the free space with He, the samples were outgassed at 250°C. for 7 hours. Because of the very slow diffusion of the hydrocarbon adsorbates into the raw and devolatilized anthracites, 24 hours was allowed to reach equilibrium for each adsorption point. For the activated samples, a one hour equilibration time was found sufficient. The adsorbates used, $n\text{-C}_4\text{H}_{10}$, $\text{iso-C}_4\text{H}_{10}$, and $\text{neo-C}_5\text{H}_{12}$, were obtained from the Matheson Co. and were of greater than 99.9% purity.

Results and Discussion

It was decided to activate anthracite of micron size in this study in order to attain the optimum in uniform particle activation and to decrease adsorption equilibration time to a minimum. Walker and co-workers (14) discuss the effect of particle size on non-uniformity of gasification. Kawahata and Walker (12) show that the specific pore volume of activated anthracite increases with decreasing particle size in the range 16 to 150 mesh.

Unfortunately, however, the handling of 6 μ anthracite during activation proved to be a problem. Initially, activation in a fluid bed apparatus, which was previously used successfully to react 100x150 mesh anthracite (15), was attempted. Excessive carry-over of the anthracite from the reactor as a result of continuous agglomeration and de-agglomeration made the use of fluidization impractical. In the case of the down-flow fixed bed reactor which was used for activation, it became evident that channeling of the gas was a problem. This apparently resulted in non-uniform reaction through the bed. That is, from the total per cent burn-off and the change in apparent density of anthracite during a run, the fraction of activation which took place within the anthracite particle (as opposed to removing external volume and thereby decreasing particle size) could be estimated. For the seven activation runs made, the percentage of internal activation varied widely, up to 100%, with no trend being found with changing activation temperature between 750 and 840°C. Results for only the sample with 100% internal activation are given here, to show under the best conditions what type of molecular-sieve properties activated anthracite can have.

The activated sample to be considered here, was reacted at 840°C. for 23.5 hours to 34.8% burn-off. Figure 1 shows the isotherms for the adsorption

of hydrocarbons on this sample. The isotherms can be closely approximated by the Langmuir equation, from which monolayer adsorption volumes can be estimated. These volumes for the activated and raw anthracite are given in Table I. Monolayer volumes for the devolatilized anthracite are not given, since they were very small and could not be accurately measured. For $n\text{-C}_4\text{H}_{10}$ adsorption at a relative pressure of 0.3, the volume adsorbed on the devolatilized anthracite was roughly 10% of that adsorbed on the raw anthracite. This indicates significant closure and contraction of pores upon heating of the raw anthracite to 950°C . Such a result has been previously reported upon the heat treatment of bituminous chars to higher temperatures (16).

From Table I, it is seen that the area available to the hydrocarbons is sharply increased upon activation, as expected. Of more importance, is the fact that the adsorption rate is markedly increased and that wide differences in the pore area available to the hydrocarbons still exist.

Table II summarizes the results for the apparent and He densities and total open pore volume on a m.m.f.b. To place the density results on a m.m.f.b., the apparent and He density of the mineral matter in all samples was taken as 2.7 g./cc. (17). The total open pore volume is considered to be the volume in pores $< 1000 \text{ \AA}$ and $> 2.5 \text{ \AA}$ in diameter. The lower limit is set by the size of pore into which He can diffuse at a significant rate at 30°C . (18).

On the basis of these results, the nature of the molecular pore system in the anthracites can be clarified further. From Hg porosimeter data on anthracite activated to 38% burn-off, it has been shown that about 94% of the total open pore volume is located in pores $< 28 \text{ \AA}$ in diameter (12). According to the Kelvin equation, pores of up to ca. this diameter will be filled by the hydrocarbons studied at a relative pressure of 0.3. Therefore, the assumption is made that the volumes of hydrocarbon adsorbed at a relative pressure of 0.3 are located in pores between a lower limit (below which the hydrocarbon will not enter) and 1000 \AA . Then, by subtracting these pore volumes from the total open pore volume, distribution data in the molecular pore size range can be determined. In agreement with Breck and co-workers (19) and others, the minimum effective pore size into which a hydrocarbon can penetrate is taken as the diameter of the circumscribed circle of minimum cross-sectional area of the hydrocarbon molecule. These minimum dimensions are 4.9, 5.6, and 6.5 \AA for $n\text{-C}_4\text{H}_{10}$, $\text{iso-C}_4\text{H}_{10}$, and $\text{neo-C}_5\text{H}_{12}$, respectively.

These results are summarized graphically in Figure 2. It is seen that even though the total open pore volume is increased on devolatilization (presumably by volatile matter release unblocking pores), the amount of pore volume available to $n\text{-C}_4\text{H}_{10}$ and larger hydrocarbons sharply decreases. Comparing the volume distributions for the raw with the activated anthracite, it is seen that in spite of a large increase in total pore volume upon activation, the pore volume between 2.5 and 4.9 \AA has decreased. This would suggest that there is little pore volume below 4.9 \AA to be opened up by additional burn-off of this anthracite. It is to be emphasized that the volume reported below a minimum effective pore size would be expected to increase with increasing adsorption temperature, because of activated diffusion and an increasing magnitude of vibration of the atoms around a pore opening.

It is of interest to compare the activated anthracite with Type A synthetic zeolite pellets for adsorption of $n\text{-C}_4\text{H}_{10}$ and $\text{iso-C}_4\text{H}_{10}$ (19). At room temperature, the 5A zeolite has a capacity of ca. 50 cc. $n\text{-C}_4\text{H}_{10}$ /g. (S.T.P.) and 2 cc. $\text{iso-C}_4\text{H}_{10}$ /g. It is thought that the adsorption of

iso-C₄H₁₀ primarily occurs on the clay binder holding the small zeolite particles together in the pellet. The ratio of gases adsorbed is ca. 25. In contrast, the activated anthracite has a capacity of ca. 110 cc. n-C₄H₁₀/g. (m.m.c.b.) and 40 cc. iso-C₄H₁₀/g. The ratio of gases adsorbed is ca. 2.8. Pelletizing the anthracite for use in fixed bed operations would be expected to lower both the adsorption capacities and separation ratio. It is obvious, then, that this activated anthracite sample does not show the sharp molecular sieve effect demonstrated by the zeolite. This is to be expected, since a range of molecular pore sizes is present in the raw and activated anthracite. Nevertheless, because of the relatively low cost of activated anthracite, it may have possible applications for rough separations in conjunction with zeolites.

Acknowledgment

We wish to acknowledge the financial support of the Coal Research Board of the Commonwealth of Pennsylvania for making this research possible.

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Table I

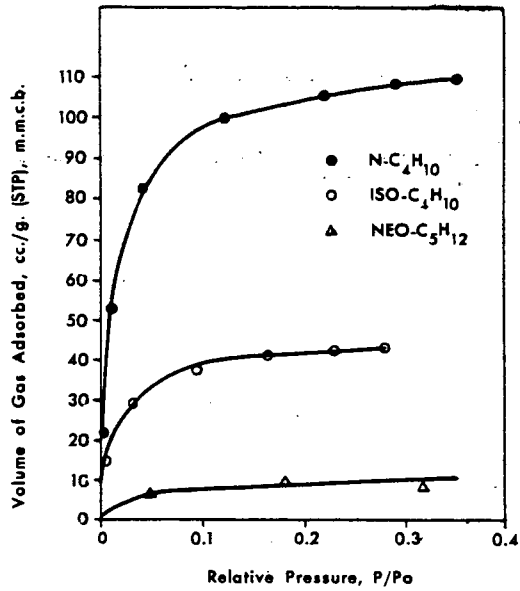
Monolayer Volumes for Different Hydrocarbons
on Raw and Activated Anthracite (m.m.f.b.)

	V_m , cc./g. (S.T.P.)		
	<u>n-C₄H₁₀</u>	<u>iso-C₄H₁₀</u>	<u>neo-C₅H₁₂</u>
Raw	12.6	8.6	2.3
Activated	134	54.5	15.5

Table II

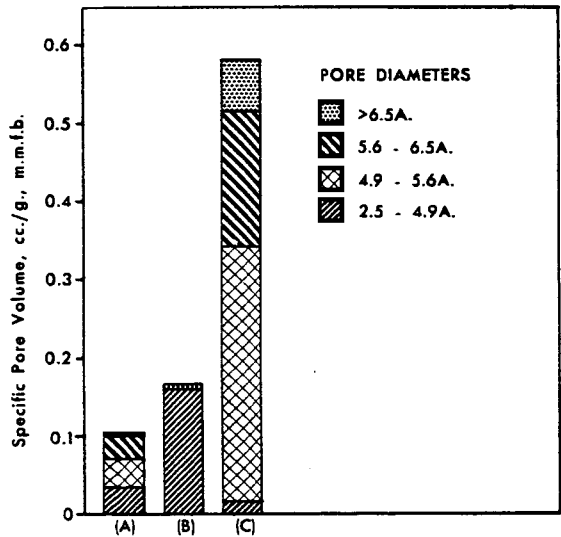
Densities and Total Open Pore Volume in Raw,
Devolatilized, and Activated Anthracite (m.m.f.b.)

	<u>App. Density</u> <u>g./cc.</u>	<u>He Density</u> <u>g./cc.</u>	<u>Total Open Pore</u> <u>Volume cc./g.</u>
Raw	1.24 ₅	1.43 ₈	0.10 ₈
Devolatilized	1.51 ₀	2.01 ₀	0.16 ₅
Activated	0.95 ₇	2.15 ₆	0.58 ₁



HYDROCARBON ADSORPTION AT 30°C.
ON ANTHRACITE ACTIVATED TO 34.8%
BURN-OFF AT 840°C.

Figure 1



PORE VOLUME DISTRIBUTIONS IN RAW
(A), DEVOLATILIZED (B) AND ACTIVATED
(C) ANTHRACITES

Figure 2

Factors Affecting the Upgrading of Iron Oxide Derived From Fly Ash

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Introduction

The iron oxide present in fly ash can be removed by magnetic separation methods. The material so obtained has possible useful applications as a heavy media agent in coal preparation and as a raw material for the steel industry. In order to meet the various specifications of the materials now used in these processes, the fly ash-derived iron oxide must be further upgraded. This paper describes some of the problems encountered in upgrading the iron oxide material.

A. Separation of Iron Oxide from Fly Ash

Iron oxide can be removed from fly ash by either wet or dry magnetic methods. Typical magnetic separations systems which could be applied to this process are shown schematically in Figures 1 and 2.

The wet process (Figure 1) involves pumping a fly ash slurry into a unit containing a magnetic drum. The magnetic iron oxide and associated material are collected from the drum, and the collected material is passed through a similar unit for further refining. The non-magnetic material is transported to a disposal area.

The dry process also uses a rotating magnetic drum. The initial separation produces middlings and tailings fractions, which are discarded, and a crude iron oxide fraction which must be further refined by passing through another magnetic unit.

The iron oxide so obtained is similar in physical and chemical characteristics (Table 1) to commercially available magnetite and therefore can be used, in some cases, as a heavy media agent without further processing.

B. Processing of Iron Oxide for Use as a Heavy Media Agent

The important factor in the use of fly ash-derived iron oxide as a heavy media agent is the magnetic content of this material. The total magnetics should be as high as possible in order to have high recovery rates at the preparation plant, thereby keeping the consumption of iron oxide per ton of coal at a low rate.

Commercially available magnetite contains 94 percent magnetic material. Samples of iron oxide from fly ash can be produced containing 90 percent magnetics, however this requires further processing of the iron oxide in another magnetic unit, or alternately by crushing the iron oxide to liberate the magnetic material and subsequent magnetic separation to collect the magnetic fraction.

This latter process serves another purpose, namely, that of producing a finer sized material. Heavy media washers of different designs require magnetic material

of different size consists for efficient operation. Certain washers can use the fly ash-derived iron oxide as it is produced from the fly ash; others require a finer material. However, further grinding reduces the total magnetics content in the iron oxide. This occurs because non-magnetic materials are present in the iron oxide and are liberated by the grinding process. The reduction in total magnetics can be as much as several percent. Detailed comparison tests are yet to be made on this phase of the project.

C. Upgrading Iron Oxide for Use as a Raw Material in the Steel Industry

The object of this phase of the program was to refine the iron oxide to obtain a fraction having the highest possible iron content while maintaining a low silica and aluminum content. Considerable attention was therefore focused on the analysis of the iron oxide material. Methods of analysis were developed to determine iron, silicon and aluminum.

Several different refining procedures were attempted.

1. The iron oxide removed from the fly ash was pulverized until 90 percent passed a 325 mesh screen. The crushed material was then washed with water several times; after each washing the iron oxide was allowed to settle and the lighter material removed by decantation. This method did not increase the iron content nor did it decrease the silica content, however the aluminum content was reduced from 6.0 percent to 3.7 percent.

2. A second attempt at purification was attempted using the following method. The iron oxide was pulverized to 98 percent through a 325 mesh screen. The magnetic iron was removed by a dry magnetic method and then processed by specific gravity separations at 2.95 specific gravity. This method also did not improve the iron or silica contents, however it decreased the aluminum to 0.3 percent.

The results of these experiments showed that the iron and silica are intimately combined in such a form that grinding and washing will not make possible a separation. This combination is described as "silicated iron oxide" and has an iron-to-silica ratio of 4.6 to 1.

3. A third attempt at reducing the silica content was attempted. This method involved crushing the original, unprocessed fly ash to 98 percent through a 325 mesh screen, however when the resultant material did not yield any iron oxide when magnetic separations were attempted. The magnetic properties of the iron oxide apparently had disappeared.

These results led to a closer investigations of the physical and chemical characteristics of the fly ash.

D. Analysis of Iron Oxide for Iron Content

No standard wet analytical method for iron in fly ash was available for use in this work. Initially, the ASTM methods recommended for cement were used in which the iron was extracted from the fly ash by hydrochloric acid. From the color of, and microscopic examination of, the residues, it was suspected that all of the iron was not extracted by hydrochloric acid. Sodium carbonate and caustic fusions were attempted and gave higher results than the hydrochloric acid extraction (Table 2). However, it was again suspected that some of the iron had not been dissolved. Hydrofluoric acid extraction of the samples was then attempted and gave results which were consistently reproducible. The hydrofluoric acid extraction method gave the highest results.

It was believed that the problems with the analyses and processing of the fly ash-derived iron oxide were associated with the silicated iron material. Microscopic examination supported this belief.

Pollen amounts of (a) fly ash, (b) the residue from the magnetic separation process and (c) the magnetic iron oxide were examined and photographed under a microscope at 200 and 400 magnification using transmitted light.

Fly ash is formed at high temperatures during the combustion of pulverized coal. At these high temperatures, the ash forming constituents of the coal melt, fuse, and form spherical masses, in most cases (Figure 3).

The spherical particles containing iron oxide are essentially magnetic (Figure 4) and can be removed by magnetic processing.

Residues from the magnetic separation are essentially devoid of spherical iron bearing particles (Figure 5); however, a fair amount of iron oxide remains as ragged, irregularly-shaped particles, some of which have a cellular appearance (Figure 6). This material is believed to be thermally decomposed pyrite which had originally replaced fusain in the coal. This pyrite was thermally decomposed by the combustion process but did not fuse into the spherical mass which is typical of fly ash particles. This material may not be magnetic.

Examination of the magnetically separated iron oxide shows a great abundance of spherical particles, all of which are not pure iron oxide. Some of this material is the previously mentioned "silicated iron oxide". This silicated material appears to exist in two forms, one in which the magnetic iron oxide occurs as discrete particles imbedded in a spherical mass of silica (Figure 7), the other as a solid core of magnetic iron oxide surrounded by a siliceous mass (Figure 8).

While this material can be readily separated from the fly ash by magnetic methods, the associated siliceous material is also removed. This unfortunately is the major problem encountered in upgrading the iron oxide.

Future work on this project will be concerned with development of improved crushing and separation methods for upgrading the iron oxide to meet specifications for new, as well as existing, process applications.

Summary

Upgrading iron oxide derived from fly ash is complicated by the physical state of the iron as it occurs in the fly ash. The "silicated" state of the iron also presents problems in analysis. Ordinary crushing of the material to release the iron embedded in the silica has not been found to be an effective means to upgrade the iron oxide. The silica content remains unchanged and the magnetic content decreases. Further experimental work is necessary to achieve the desired degree of upgrading.

Acknowledgement

The photomicrographs were taken by Richard Moses, BCR petrographer.

TABLE 1. COMPARATIVE DATA ON FLY ASH-DERIVED IRON OXIDE
AND COMMERCIAL MAGNETITE

Screen Analysis - Percent Retained		
Screen Size	Iron Oxide	Commercial Magnetite Grade 2
+ 50 mesh	0.15	3.8
50 x 70 mesh	0.25	4.4
70 x 100 mesh	0.70	4.4
100 x 140 mesh	0.35	6.2
140 x 200 mesh	6.35	7.6
200 x 325 mesh	26.80	13.5
- 325 mesh	62.40	64.5

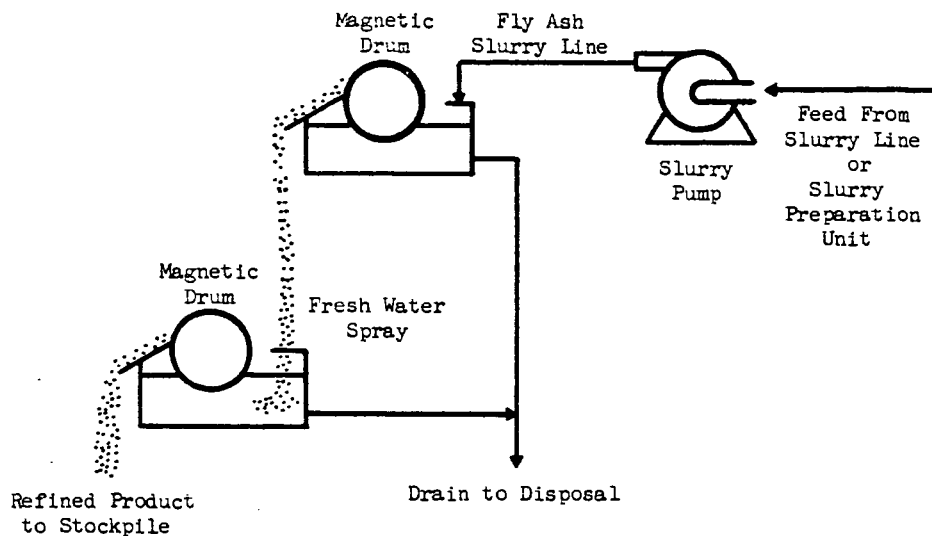
Approximate Chemical Analysis, Percent by Weight		
	Iron Oxide	Commercial Magnetite
Iron	57	62
Silicon	6	2
Manganese	0.8	0.2
Aluminum	3	4
Calcium	0.2	0.50
Magnesium	0.04	1.50
Moisture	0.10	0.50

Physical Properties		
Specific gravity	3.82	4.80
Magnetics	90%	94%

TABLE 2. COMPARISON OF RESULTS OF IRON ANALYSES
USING VARIOUS METHODS

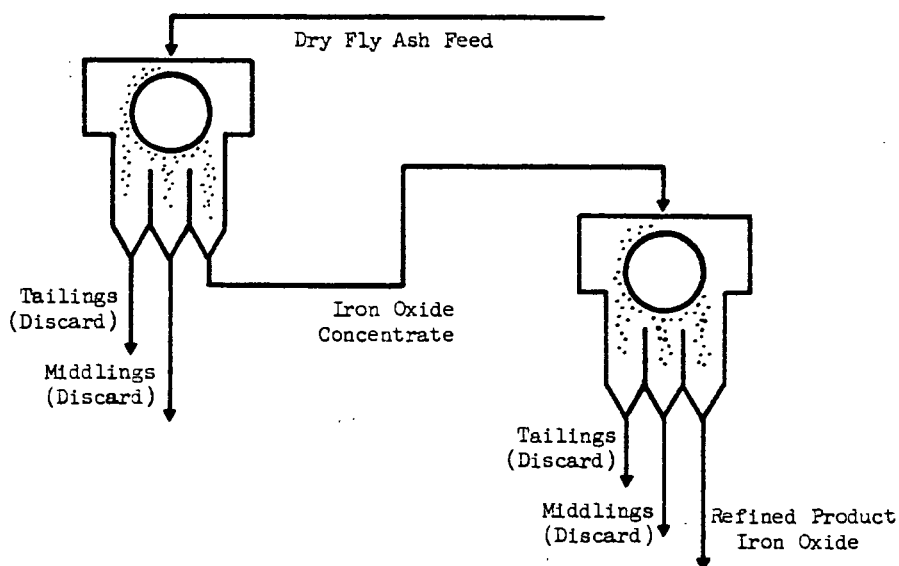
Sample	Sodium Carbonate Fusion *	Caustic Fusion		Hydrochloric Acid Extraction	Hydrofluoric Acid Extraction
		Initial	Secondary		
	%	%	%	%	%
1	5.9	8.7	-	6.0	11.6
2	14.9	11.0	14.9	3.2	18.4
3	4.5	5.7	-	2.7	8.0
4	4.6	8.1	-	7.2	11.1
5	36.8	36.7	4.5	41.3	44.1

* Results reported by another laboratory.



Bituminous Coal Research, Inc. 2508G1

Figure 1. Wet Magnetic Separation Process for Recovering Iron Oxide From Fly Ash



Bituminous Coal Research, Inc. 2508G2

Figure 2. Dry Magnetic Separation Process for Recovering Iron Oxide From Fly Ash

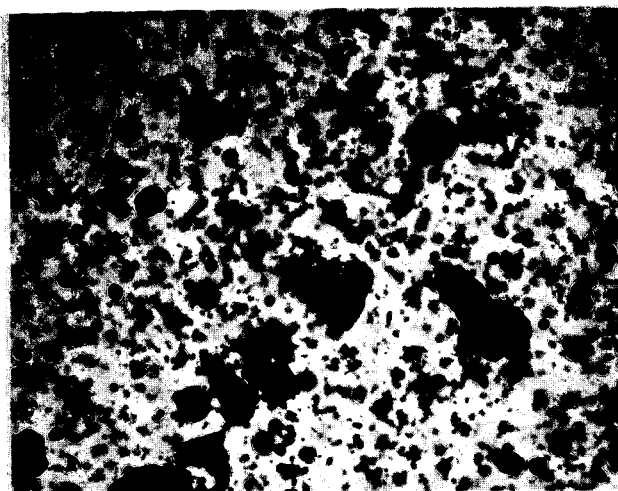


Figure 3. 2508P1
Fly Ash from Mechanical Dust Collector of an
Operating Power Station Burning Pulverized
Coal (200x)

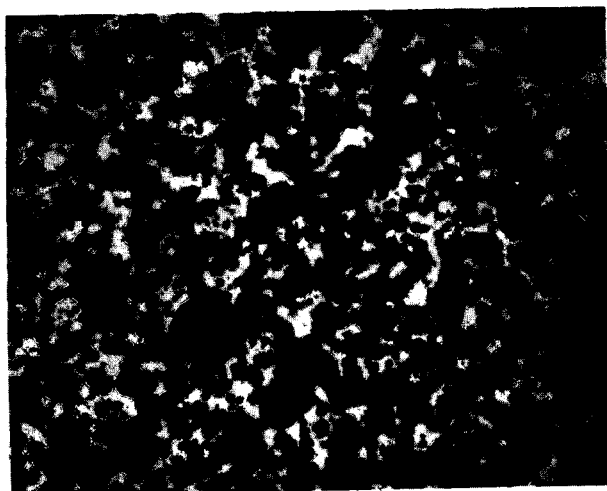


Figure 4. 2508P2
Iron Oxide Magnetically Separated from
Fly Ash (200x)

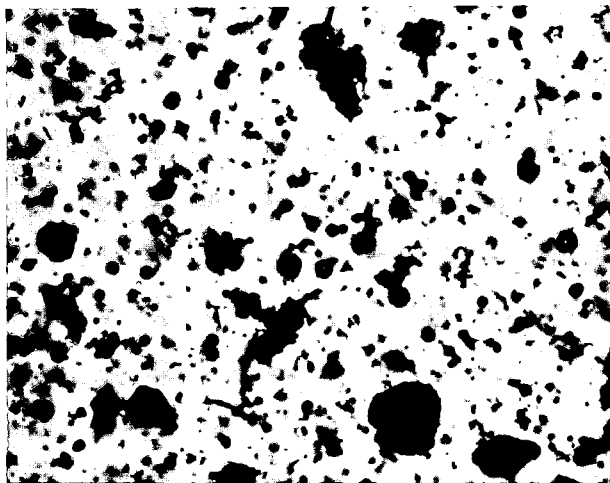


Figure 5. 2508P3
Non-Magnetic Residue from Magnetic Separation
of Fly Ash (200x)



Figure 6. 2508P4
Unfused Iron Oxide (top center) in Non-Magnetic
Fraction of Fly Ash (400x)

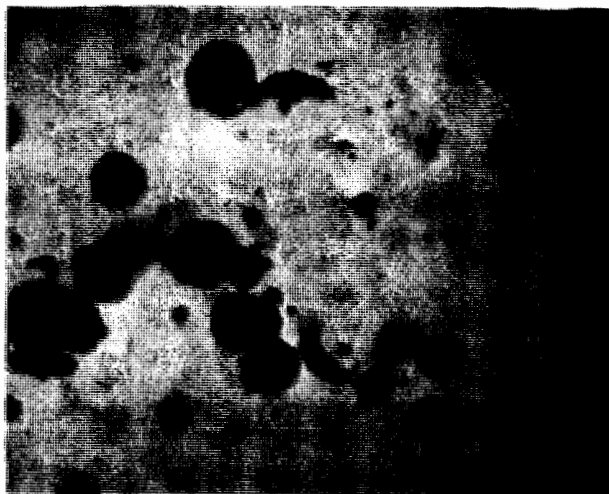


Figure 7. 2508P5
 Discrete Iron Particles Enclosed in Siliceous Mass
 Found in Magnetic Fraction of Fly Ash (200x)

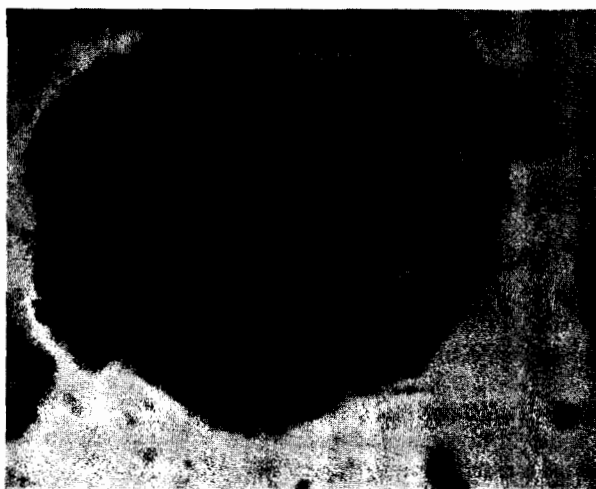


Figure 8. 2508P6
 Iron Oxide Sphere Enclosed by Siliceous Mass Found
 in Magnetic Fraction of Fly Ash (400x)

COAL-IN-TAR DISPERSIONS AS HIGHWAY CONSTRUCTION MATERIALS

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Introduction

When bituminous coal is digested in a mixture of coal tar pitch and high-boiling tar oil, at temperatures in the approximate range of 300-320 C., little or no chemical decomposition of the coal occurs and the coal-modified pitch, which appears to be a colloidal dispersion of the coal as coal in the pitch-oil mixture, has temperature susceptibility characteristics better than those of the original pitch, i. e., it softens less at elevated temperatures and hardens less as temperatures are decreased.

For about thirty years coal-modified pitches have been used very successfully as hot-applied enamels for the protection against corrosion of steel structures, marine piling and underground pipe lines for the transmission of oil, gas and water. Because of their superior temperature susceptibilities they are better for such purposes than coal tar enamels made by usual procedures.

Less successful have been various attempts to use coal-in-tar dispersions for other purposes for which it might be expected - because of their improved temperature susceptibilities - that they would be better than coal tar or asphaltic materials ordinarily used for such purposes. Of particular interest in this connection are some major efforts that have been made in Great Britain and, most recently, in South Africa and the United States to employ coal-modified tars as binders for bituminous highway pavements.

Bituminous Road Binders - Tar vs. Asphalt

Binders used in pavements of the bituminous concrete type are made either from petroleum, by the vacuum or steam reduction of petroleum residuals, or from coal tar by straight distillation to the required consistency or the fluxing of coal tar pitch with tar oils. In the United States unfilled hot-mix binders of petroleum origin are called asphalts, paving asphalts or asphalt cements whereas in Great Britain and various other countries they usually are referred to as bitumens, asphaltic bitumens or petroleum bitumens to distinguish them from natural or synthetic mixtures of bitumens and fillers that are called asphalts. In the following discussions unfilled asphaltic binders will be designated as paving asphalts or asphalt cements. Coal tar binders, made either by straight distillation or the fluxing of pitch with tar oils, will be designated as tar cements.

In general, asphalt cements have better temperature susceptibilities and are less volatile at mixing, paving and atmospheric temperatures than tar cements. On the other hand, tar cements have better adhesion to most road aggregates on prolonged contact with water; are more resistant to chemical alteration by water; are dissolved or softened less by petroleum lubricating oils, jet fuels and gasoline; produce more permanently skid resistant pavements and are not as susceptible to

56. age hardening within pavements that are densely graded or tightly sealed so that oxidation or evaporation of the binder is minimized.

Experience, both in the United States and abroad, has shown that excellent pavements of the bituminous concrete type can be constructed either with asphalt cements or with tar cements. However, different mixing and paving techniques are required. For example higher aggregate drying and mixing temperatures are needed when asphalt cements are used to insure substantially complete removal of all moisture from the aggregate and to fluidize the asphalt cement sufficiently to insure rapid and thorough coating of all aggregate particles. Lower temperatures should be used for tar cements to avoid excessive volatilization of tar oils with consequent hardening of the binder. With tar cements it is possible to use lower aggregate and mixing temperatures because they will tolerate considerably more moisture in the aggregate than asphalt cements. Also because tar cements are sufficiently fluid at the lower temperatures to insure satisfactory mixing and paving operations.

Another important difference in the preferred construction techniques for pavements containing tar or asphalt cements has to do with aggregate gradations. For best results, tar cements should be used with densely graded aggregates so that the finished pavements will be substantially voidless (3-5% residual air voids). Should a slight excess of tar binder in the mixture cause flushing of binder to the surface, the thin film of tar cement, on hardening, will be worn off by traffic. This will expose the angular particles of aggregate to produce a skid-resistant pavement surface. Because of the density of the compacted mixture, evaporation of oils from thin tar films below the pavement surface is prevented and little or no alteration of the tar binder occurs. On the other hand, a somewhat more open aggregate gradation may be used with asphalt binders. If sufficiently dense mixes are used so that flushing occurs, this must be held to a minimum to avoid the development of slippery surfaces when wet.

Methods For Improving Tar and Asphalt Binders

Various methods have been used or tried with a view to improving both tar and asphalt binders. In the case of asphalt cements such efforts have been directed mainly toward better adhesion to aggregates in the presence of water by the admixture of certain chemicals or tar oils, greater skid resistance by the addition of coal tar pitch and less "age hardening" through the use of better manufacturing procedures including the selection of raw materials.

Efforts to improve tar cements have been directed almost entirely toward the improvement of their temperature susceptibilities. The method most commonly employed, especially in Great Britain and Germany, has been the addition of paving asphalts to tar cements. Usually the asphalt content of such mixtures has been about 15-25 per cent but as high as 40 per cent has been used with some mid-temperature coal tars such as are produced by vertical retorts. In the latter case some improvement in binding capacity as well as temperature susceptibility is expected. As yet, this method has not been used extensively in the United States, largely because the asphalt cements produced in this country vary widely with respect to compatibility when mixed with tar cements derived from high-temperature, coke oven coal tars. When stored and used at the high temperatures employed at hot-mix paving plants such mixtures may or may not segregate or sludge depending upon the type of petroleum from which the asphalt was derived and the method of reduction used in its manufacture.

The addition of small amounts of synthetic rubber to coal tar cements is another method that has been used to some extent for improving their temperature susceptibilities. They have been used most extensively at airports where asphalt surfaces have been damaged excessively by jet fuel spillage. Aprons or runways constructed with rubberized tars, in addition to being jet-fuel resistant, deform less at high temperatures and are less likely to crack at low temperatures under heavy loads and impacts. However, the addition of rubber to the tar does not reduce its volatility and the rubberized tar binder must be stored and used at the lower temperatures recommended for usual tar cements.

Another possible method for improving tar cements is the one that will be reviewed in this paper, namely, coal-in-tar dispersion.

The Dispersion of Coal as Coal In Tars and Oils

The fact that coal as coal, at temperatures below those at which chemical decomposition of the coal begins, can be dissolved or colloiddally dispersed in cyclic hydrocarbons such as coal tar, water gas and oil gas tars, or chemicals, oils and pitches derived therefrom was recognized, almost forty years ago, by Harold J. Rose and William H. Hill. From investigations started about 1924 in the Mellon Institute laboratories of the Koppers Company, Pittsburgh, Pennsylvania, they found that at digestion temperatures preferably in the approximate range of 300 - 320 C, bituminous coal appears to dissolve in tars and tar oils, or their combinations, without chemical decomposition of the coal. The end product is a pitch-like material which, depending upon the kinds and proportions of ingredients used, may have temperature susceptibilities substantially better than those of pitches made from coal tar, water gas tar or oil gas tar by usual distillation procedures. Presumably, as the digestion product cools to atmospheric temperature, the coal, which had dissolved in the digestion medium at the digestion temperature, comes out of solution to form a gel-like, colloidal dispersion of the coal in which, except for insoluble mineral ash, no particles of the original lump or pulverized coal are visible with a microscope at magnifications of 400 - 500.

The laboratory investigations of Rose and Hill resulted in the issuance of several United States and foreign patents to them with assignment to The Koppers Company. Their first patent¹ of this kind was issued in Great Britain in 1928. The laboratory studies were followed by extensive pilot plant and field investigations in which the Research Division and the Tar Products Division of The Koppers Company collaborated. Many possible outlets for coal-in-tar dispersions were investigated but most successful was the development by Koppers of superior enamels and coatings for steel structures, marine piling and transmission pipe lines for oil, gas and water. Their superiority over other coatings used or proposed for use on buried pipe lines was established by service tests conducted jointly by The American Petroleum Institute², The American Gas Association and The U.S. Bureau of Standards. In those tests, which were started in 1930 and concluded ten years later, pipe nipples coated with the various test materials were buried at fourteen locations in the United States and specimens were inspected at yearly intervals. Koppers' coal-digestion product, designated as Komac, behaved so favorably that its commercial production was started by the Wailes, Dove, Hermiston Corporation, maker of Bitumastic enamels and coatings, following the disclosure of manufacturing procedures to them by Koppers. Other commercial uses for coal digestion products were tried, less successfully, by the Koppers Company but they did not include highway construction or maintenance materials, except for a few field tests that were made

58. with coal digestion pitches as brick and concrete pavement joint fillers. The first efforts to use coal-in-tar dispersions as road construction materials were made in Great Britain.

British Experiments with Coal-modified Tar Road Binders

In 1929 a British patent³ was issued to the South Metropolitan Gas Company, London, (Pickard and Stanier) on a process for making a tar product with improved "temperature-mobility" characteristics. As in the case of the British patent¹ issued to Rose and Hill (Koppers) in 1928 the process consisted in dispersing coal in tar at about 300 C but the South Metropolitan Gas Co. patent was directed specifically toward making an improved road material or a substitute for mixtures of tar and asphaltic bitumen (paving asphalt) for road-making and like purposes by dispersing not more than fifteen percent of bituminous coal in coal tar. Tar suitable for the purpose was made either by partial distillation of crude coal tar to drive off lighter oils which would be lost during the digestion process at approximately 300 C or by distillation of the crude coal tar to pitch and subsequent adjustment of the latter by the addition of tar oils.

A second British patent⁴ was issued to South Metropolitan Gas Company (Herbert Pickard) in 1930. It claimed the mixing with stone of a tar binder of the coal dispersion type described in the preceding patent to produce a road surfacing mixture of the hot-mix, hot-lay, asphaltic concrete type.

Detailed information gained from their investigations was furnished by Evans and Pickard in a treatise⁵ published by South Metropolitan Gas Company in 1931. It contained a large amount of valuable information about (1) The Relationship Between Temperature and Consistency of Coal Tar (2) The Preparation Of Asphaltic-Like Substances From Coal Tar and (3) The Consistency of Pitch-Like Substances.

According to personal communications recently received by the author, additional experiments involving the use of coal-in-tar dispersions were made in Great Britain in 1945 by the South Eastern Gas Board (formerly known as South Metropolitan Gas Company). As in the earlier experiments, the purpose of the tests was to substitute coal-in-tar dispersions for tar-asphalt blends for dense tar surfacings. Asphalt suitable for the purpose was expensive and in short supply at that time, but shortly thereafter it became more plentiful again and work on the coal dispersion binders was discontinued.

Also, according to personal communications, the Coal Tar Research Association of Great Britain made additional tests in 1956 that were directed toward the improvement of tar binders for use in dense surfacings on airfields. Coal was digested in a mixture of coal tar pitch and topped coke oven tar heavy oil. Laboratory tests were said to be encouraging but, when small test sections of pavement were laid, fuming was reported to be somewhat excessive and large scale service tests were not attempted.

Coal-Modified Tar Binder Experiments in South Africa

In a paper⁶ published in October 1959, Dr. H. Karius and Dr. E. J. Dickinson reported the results of investigations which they had conducted in Pretoria, South Africa as a part of the program of research of the Bituminous Binder Research Unit, National Institute for Road Research. The purpose of the work was "to find means of decreasing the temperature susceptibility of viscosity and the brittleness at low

temperatures of road tars derived from steel works coke-oven crudes at least to the level of that of straight-run petroleum bitumens". Concerning coal-in-tar dispersions, their observations may be summarized as follows:

1) Road binders with temperature susceptibilities of viscosity and brittleness at low temperatures similar to those of bitumen (asphalt) resulted from the digestion of certain types of South African coal in tar especially in concentrations of 10 - 15 percent by weight.

2) The combined effect of coal and synthetic rubber on tar or pitch is greater than the sum of their separate effects. With coal present, the amount of synthetic rubber needed to equal the flow characteristics of asphalt is minimized or, by dispersing both coal and synthetic rubber in tar or pitch, flow characteristics superior to those of asphalt are obtainable. However, when coal is present it is necessary to add a substantial amount of high-boiling coal tar oil to reduce the viscosity of the dispersion when it is to be used for road construction purposes.

3) Either the GR-S (styrene-butadiene copolymer) or the Buna N (butadiene-acrylonitrile) type of synthetic rubber may be used in conjunction with coal to improve the rheological properties of tar but the GR-S type must be added in latex form.

4) Synthetic rubber, especially of the Buna N variety, when added to pitch-asphalt mixtures, appeared from laboratory tests to act as a stabilizing agent so that any pitch-to-asphalt ratio might be used without causing incompatibility in the heated mixture. Also heat-stable pitch/oil/coal/asphalt/rubber blends were prepared by mixing a coal/pitch/oil blend with a rubber/asphalt blend. Both natural rubber latex and Buna N latex were used in this manner.

Heat stable blends of the types mentioned above were described in a South African patent application⁷ filed in June 1958 by Karius and Dickinson and assigned by them to the South African Council for Scientific and Industrial Research.

During and after the laboratory investigations of Karius and Dickinson, single-seal applications of tars and asphalts, with and without the addition of coal and polymers, were made on highways near Pretoria so that they might be compared and evaluated under actual service conditions. Reports on the outcome of those field tests have not yet been published.

American Investigations of Coal-Modified Tar Road Binders

Curtiss-Wright and Kentucky Highway Department Tests

The most recent attempt to develop improved binders for bituminous concrete pavements by the dispersion of coal in tars and oils was made in the United States. In the Fall of 1958 the Curtiss-Wright Corporation, whose research and development laboratories were located at Quehanna, Pennsylvania in the heart of a bituminous coal mining region, decided to explore this possibility after conferring with members of the U.S. Bureau of Mines, Bituminous Coal Research Inc. and others. Because of the successful use of coal-in-tar dispersions as pipe line enamels, which the Koppers Company was known to have developed following the researches of Rose and Hill, it was thought that similar techniques could be employed for the production of improved road binders.

Curtiss-Wright was aware of the early work along similar lines that was done by the South Metropolitan Gas Company in England but was not aware of the more recent experiments by the South Eastern Gas Board and by the Coal Tar Research Association in Great Britain or by Karius and Dickinson in South Africa.

Articles describing those investigations had not yet been published. In fact, nothing was found in the literature which would indicate that anyone had commercially produced satisfactory coal-modified tar binders for highway construction purposes.

Laboratory tests which began at Quehanna in January 1959 were continued, without interruption, for almost two years. During the latter half of 1959 they were supplemented by pilot plant and full scale highway service tests in Kentucky in which the Curtiss-Wright Corporation and the Kentucky State Highway Department collaborated. The laboratory work at Quehanna and also the design, construction and operation of the Kentucky pilot plant was, for the most part, directed by Mr. S. H. A. Young, Chief Development Engineer of the Curtiss-Wright Research and Development Department; the Project Leader at Quehanna during most of the two year period was John Horai; Frank Soriero was manager, for Curtiss-Wright, of the pilot plant and field operations in Kentucky and E. O. Rhodes assisted Curtiss-Wright in a consulting capacity both at Quehanna and in Kentucky. The Kentucky mixing and paving operations were supervised by the Highway Research Laboratory, Kentucky Department of Highways, of which Dean D. N. Terrell was the Director and Mr. W. B. Drake the Associate Director. An independent study and evaluation of the various binders produced and used in the Kentucky experiments was made in Washington, D. C. by The U.S. Bureau of Public Roads. The results of the Quehanna, Kentucky and Washington investigations were reported at the 41st annual meeting of the Highway Research Board, Washington, D. C. in January 1962 in preprints of papers by Rhodes⁸, Drake⁹, and Halstead, Oglio and Olsen¹⁰. Following is a condensed summary of the information furnished by Rhodes concerning the Quehanna and Kentucky experiments.

Preliminary Quehanna Investigations

During the first six months of 1959 many laboratory tests were performed by Curtiss-Wright at Quehanna, Pennsylvania in which coal dispersions were made with different coals, tars and oils under varying conditions of time, temperature and pressure. From a large number of formulations tried, two were selected for comparison with a typical 70-85 penetration asphalt cement and with a representative sample of tar cement meeting ASTM specifications for RT-12 grade road tar. The latter was made by straight distillation of high temperature, coke oven coal tar. One of the coal dispersions, (CW-II), contained 10.8% bituminous coal from the Freeport seam near Quehanna, Pa. and 89.2% of the RT-12 tar cement. The other (CW-III) contained 11.4% Freeport seam coal, 64.4% RT-12 tar cement and 24.2% high-boiling coal tar oil (m. m. t. 5% distillate to 315 C and 70-75% residue at 355 C). In each case the coal, dried and pulverized to pass 100% through a 100 mesh sieve, was mixed with the RT-12 road tar or RT-12 plus high-boiling coal tar oil, the mixture was heated, with agitation, to 600 F (315.5 C), maintained at that temperature for one hour, cooled to 400 F and withdrawn from the autoclave into containers. The autoclave was vented to the atmosphere throughout the run. Neither pressure nor reflux was required to obtain complete dispersion of the coal in the tar or mixture of tar and oil.

Laboratory tests indicated that each of the coal-modified tar cements (CW-II and CW-III) should be superior to the 70-85 penetration asphalt cement with respect to insolubility in jet fuels and also adhesion to aggregates in the presence of water; furthermore, it appeared that they should be superior to the RT-12 grade tar cement but somewhat inferior to the asphalt cement from the standpoint of volatility at usual asphalt mixing and paving temperatures. (225-325 F).

Comparative tests on Marshall briquets made with the various binders gave the following results:

Marshall stabilities at 140 F of briquets made with the coal-modified tar cements (CW-II and CW-III) were approximately 50% higher than those of the asphalt briquets and 100% higher than the stabilities of RT-12 briquets.

Immersion in water for 96 hours at 120 F caused the Marshall stabilities of briquets made with CW-II, CW-III and RT-12 to increase 9%, 88% and 14% respectively whereas the stabilities of the asphalt briquets decreased 17%.

After heating for 72 hours at 140 F the stabilities of briquets containing CW-III decreased only 3% and impact resistance at 32 F increased 32%. The stabilities of the asphalt briquets decreased 20% and their impact resistance at 32 F decreased 26%.

The jet fuel solubility of the CW-III briquets was only 2% as compared with 38% for the asphalt briquets.

The asphalt briquets were somewhat superior to those made with coal-modified tar binders with respect to impact resistance at 32 F and evaporation loss on heating for 72 hours at 140 F.

On the whole it appeared from the preliminary Quehanna experiments, that improved binders for bituminous concrete pavements could be made by the modification of a standard grade of coal tar cement (RT-12) with bituminous coal or bituminous coal and high boiling coal tar oil. Public announcements to the effect were made by Curtiss-Wright in April 1959 and shortly thereafter they contracted with the Commonwealth of Kentucky to produce 150,000 gallons of coal modified tar cement for experimental use in that state.

Kentucky Pilot Plant

A pilot plant to make 1500 gallon batches of coal-modified tar cement was designed by Curtiss-Wright and it was installed and operated by them at Frankfort, Kentucky during the latter half of 1959. Operation of the pilot plant was as follows: RT-12 grade road tar, pulverized Kentucky coal and high-boiling coal tar oil were transferred to a 1500 gallon digester from tank cars or tank trucks; the mixture was heated as rapidly as possible to 600 F, with agitation but without reflux, and maintained at that temperature for one half hour; by means of an internal water-cooling coil the temperature was reduced to 400 F and the finished binder was transferred to storage or transports. No major difficulties were encountered in the operation of the pilot plant in this manner.

During the construction of the pilot plant fifty four coal samples from eastern and western Kentucky coal mines were analyzed and tested on a miniature scale for digestibility in RT-12 at Quehanna. Three of the samples, selected as being representative of eastern and western Kentucky coals, were made into two and three component type binders (CW-II and CW-III). The latter were mixed in varying proportions with representative samples of Kentucky aggregates to establish the optimum binder content for Kentucky Class I hot-mixes in which they were to be used. By agreement with the Kentucky Highway Research Department a binder content of 7.0 percent was first used and later changed to 6.9 percent.

During the period between August 13th and November 7th 1959 one hundred and four batches of hot-mix binder, totalling approximately 150,000 gallons were made in the pilot plant. One hundred batches (144,000 gallons) were of the three component type (CW-III) with the following average composition, 81% RT-12, 11% high-boiling coal tar oil and 8% coal; two batches (3,000 gallons) of the two component

62. type (CW-II) contained 96% RT-12 and 4% coal, and two batches (3,000 gallons) contained only RT-12 which was heated to 400 F in the digester before delivery to test sites.

Kentucky Field Tests

The CW-III type binder was delivered to fourteen test sites in various parts of Kentucky. At twelve of the sites the binder was used in 1-1/2 inch Kentucky, Class I overlays on existing black top pavements which, for the most part, had required a large amount of maintenance because of base failures or the development of slippery-when-wet surfaces. At the other two test sites the CW-III binder was used in hot-mix that was laid 2-3/4 inches thick over tar-primed soil roads in accordance with Kentucky, Class I Modified Base specifications.

The CW-II type binder was used at only one location (8 miles south of London) in a 1-1/2 inch overlay of the Class I type.

The RT-12 road tar was used in a short 1-1/2 inch Class I overlay at the above location and also in a 2-3/4 inch, Class I, modified base near Bowling Green for comparison with the CW-III type of binder.

The hot mixes were made in eleven commercial, hot-mix plants of which six were batch and five continuous. No major difficulties were encountered at any of them in the use of the coal-modified binders. Also, except for somewhat excessive fuming when paving temperatures exceeded 260 F, paving operations by nine different contractors were very satisfactory even though atmospheric temperatures varied from about 27 F to 100 F during the construction period.

However, service results from the various test pavements were not entirely satisfactory. After the first winter, which was unusually severe, considerable surface abrasion, (due in part to tire chains), and cracking was observed particularly at center joints and near the edges where the new overlays projected beyond the original pavement surfaces. Cracking was particularly noticeable at locations where the 1-1/2 inch overlays were placed on old and unstable black top pavements that had required extensive maintenance in former years. It was obvious that the overlays containing the CW-III type binder (coal, RT-12 and high-boiling oil) were too hard and brittle and did not have enough flexibility, particularly at low temperatures, for use over unstable pavements.

At the one location (8 miles south of London) where overlays containing asphalt, RT-12, and each type of coal-modified tar binder (CW-II and CW-III) could be compared under identical conditions, it appeared that the one containing only RT-12 was least satisfactory because of excessive bleeding during summer months, the section containing CW-III binder (coal, RT-12 and oil) was too brittle and inflexible and the section containing the CW-II binder, (4% coal plus 96% RT-12) compared most favorably with the asphalt control section. It appeared to have more flexibility and less brittleness at low temperatures and a greater tendency to "self-heal" in hot weather, without bleeding excessively, than the CW-III binder made with 8% coal, 81% RT-12 and 11% oil.

Soon after the test sections were laid it was apparent that the coal-modified binders should have been somewhat softer, i.e., their initial ASTM penetrations at 25 C should have been higher, a somewhat greater proportion of each should have been used in the hot-mixes, and lower mixing and paving temperatures should have been used to minimize hardening due to the evaporation or sublimation of some of the tar oils. With a view to making further improvements, the Quehanna investigations were directed along the following lines during most of 1960.

By comparing the absolute viscosities, at different temperatures, of the four binders used in Kentucky it was concluded that mixing and paving temperatures in the range of 200 - 250 should be adequate for coal-modified binders of the CW-II and CW-III types.

Ten percent dispersions of coal in RT-12 were made with a large number of coal samples from various locations in North America, South America and Japan. Their softening points (R & B) varied from 40 C to 65 C but they all appeared to have approximately the same temperature susceptibilities in the range of 25 to 32 C. For these tests, 25 gram portions of each coal were dispersed in 225 grams of RT-12 by heating the mixture, with agitation and reflux of condensable vapors, to 600 F for one hour. The results were comparable to those obtained from Quehanna autoclave and Kentucky pilot plant digestions.

Low, medium and high temperature coal tars distilled to RT-12 consistency were compared as dispersing media for Freeport seam coal. The distilled low temperature tar was unsatisfactory but dispersions made with RT-12 from two medium temperature tars compared favorably with a dispersion of the coal in RT-12 from high temperature coke oven tar.

Various polymers were added to a modified coal dispersion of the CW-III type (coal, RT-12, and oil). Included in these tests were Hycar latex, natural rubber latex, reclaimed rubber, Neoprene powder, Neoprene latex, Butyl rubber, Vistanex and Thiokol LP-3. Most of the mixtures sludged or crusted on heating at 325 F for five hours. Vistanex, Butyl rubber and Thiokol were best in this respect and appeared to effect some improvement in the temperature susceptibilities of the coal modified tars.

Three aromatic oils of petroleum origin were tried, in place of high boiling coal tar oil, as plasticizers or fluxes but were incompatible when the mixtures were heated.

Promising results were obtained by adding high-penetration, petroleum residuals (180 - 200 or 250 - 300) to a dispersion of coal in RT-12. Temperature susceptibilities, particularly in the range below 25 C appeared to be substantially improved.

A sand blast method of test described by Rhodes and Gillander in 1936¹¹ appeared to be especially suitable for measuring the brittleness of hot mix binders particularly at low temperatures.

Bureau of Public Roads Investigations

As previously stated, the U.S. Bureau of Public Roads made independent studies of the asphalt, RT-12 and coal-modified tar binders used in the Kentucky experiments. They found that the temperature susceptibility of the CW-III binder was slightly lower than that of the RT-12 but not as low as the temperature susceptibility of the Kentucky 85-100 penetration asphalt cement; the absolute viscosities of the coal-modified tar binders were intermediate between those of the RT-12 and the asphalt cement; when subjected to thin-film oven tests the losses from CW-III were somewhat lower and retained-penetrations were somewhat higher than those of RT-12 but asphalt cement was better than either in both respects; oven ageing at 140 F for 30 days caused the Marshall stabilities of briquets made with the different binders to increase as follows, RT-12 439 pounds, CW-III 2248 pounds, asphalt cement 336 pounds; development of structure or reversible hardening took place to the greatest extent in the coal modified binder (CW-III), to a lesser extent in the

64. asphalt cement and, apparently not at all in the RT-12 when thin films of each were sealed between glass plates and heated at 110 F for 13 days; immersion of quartzite briquets in water at 120 F for 18 days caused those containing CW-III to lose 8% in strength and to swell 0.2% whereas decrease in strength for asphalt briquets was 44% and swell amounted to 1.4%; unconfined compression tests indicated that the coal modified tar binder should provide higher stabilities than the asphalt cement at any temperatures encountered in service. At 0° F the stabilities of specimens containing RT-12 and CW-III were about double the stability of the asphalt specimens and were in the range of strength of Portland cement concrete. In general the Bureau of Public Roads report concluded that coal-modified tar binders, such as those made by Curtiss-Wright, should be considered as improved tars that would be expected to perform better than unmodified tars in a number of applications but normal precautions should be employed when using them rather than attempting to substitute them for penetration grade asphalts.

Conclusion

Although major efforts have been made in Great Britain, South Africa and the United States to use coal-in-tar dispersions as highway construction materials, commercial success has not yet been achieved. A large amount of important information has been contributed by the investigations conducted to date but additional work is needed particularly along the following lines.

Methods for determining the temperature susceptibilities and, particularly, the brittleness at low temperatures of bituminous, hot-mix binders that have been used by previous investigators in this field should be compared and, if necessary, a new method should be developed. A few tests by Curtiss-Wright indicated that a sand-blast method might be especially suitable and additional tests should be performed. Also better methods for evaluating and comparing hot-mixes containing asphalt and coal-modified binders should be selected or developed in order, by means of laboratory tests, to predict most accurately the service lives of the finished pavements.

Formulations for road binders of the coal-dispersion types should be further improved. Most needed in this connection are better and less expensive plasticizers for use in place of high-boiling coal tar oil. Some of the materials which should be considered in this connection are water-gas and oil-gas tars and distillates therefrom, low-temperature and mid-temperature tars and tar oils and also petroleum distillates, extracts and residues. High boiling oil from heavy water gas tar is known to have good possibilities in this connection and tests made by Karius and Dickinson and also by Curtiss-Wright indicated that soft (high-penetration) asphalts should be especially interesting.

Continuous, rather than batch digestion of coal should be tried. Heretofore batch methods have been used exclusively for the commercial, pilot plant and laboratory dispersion of coal-as-coal in tars and tar oils. However, finely pulverized coal dissolves so rapidly and completely that continuous digestion with inexpensive equipment should be practicable.

Also the use of coal modified binders in highway subgrades and bases as well as surface courses should be tried. Because of the high strengths of mixes containing them and because of their extreme resistance to destruction by water, superior adhesion to aggregates and ability to penetrate soils and damp or dusty aggregates, coal dispersions made with coal tars and tar oils should be especially suitable for subgrade and base stabilization whereas coal-in-tar dispersions containing materials such as high penetration asphalts might be more suitable for use in surface courses.

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EFFECT OF AGGREGATE ON COKING OF BINDER IN PETROLEUM COKE-PITCH MIXTURES

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During investigation of pitches, it was observed that when pitch and calcined petroleum coke were mixed together and heated at about 130°C, the paste showed striking differences; its appearance varied from wet and sticky to sandy and dry, as proportions of the two components were changed. The transition was sharp, and the binder:aggregate ratio at which it occurred varied for a number of pitches, in some cases even for pitches of similar softening points. It was also found that increasing the temperature intensified the interaction between pitch and aggregate and enhanced differences in appearance of the heated mixtures. These qualitative observations were followed by quantitative tests involving preheating steps at temperatures below 400°C followed by a coking treatment at 550°C. Several mixtures were prepared containing from 30 to 70% of -200 mesh calcined petroleum coke in increments of 5 to 10%. After thorough mixing, the mixtures were placed in porcelain crucibles fitted with a lid and the whole was imbedded in calcined petroleum coke inside a nickel crucible. After heating for 30 minutes at 200°C and 30 minutes at 300°C in a muffle furnace, the mixtures were coked at 550°C for two hours. The percentage of original pitch converted into coke was calculated from the total carbon residue corrected for the original weight of aggregate; weight loss of the aggregate itself was negligible.

FIGURE 1, illustrates the effect of preheating on the amount of pitch coke formed during the coking step. With no preheating, the yield of pitch coke remains fairly constant over the entire range of binder:aggregate ratios, and is substantially the same as the coking value of the pitch determined separately. With the mixtures preheated at 200 and 300°C, the results are quite different. For high contents, variations in pitch coke yield are not significant. However, when the pitch content decreases to a point - which we call the "saturation point" - where the mixture presumably is no longer saturated with pitch, the pitch coke yield increases suddenly up to a level at which it remains fairly constant even with further reduction in pitch content. The sharp increase in pitch coke yield coincides with the visible change in the appearance of mixtures mentioned previously.

The shape of the curve and location of the saturation point are influenced by the particle size of the aggregate as shown in FIGURE 2. The heating programme was also found to be critical, especially in the range from 200 to 400°C where the pitch is extremely mobile and shows high wetting power towards the aggregate.

The increase in amount of pitch coke formed might be attributed to the retention of increasing quantities of volatile pitch fractions as the aggregate proportion in the mix increases; however, this increase in pitch coke yield would be expected to be gradual and not as sudden as the actually observed change. On the other hand, increasing the aggregate particle size results in a flattening of the curve indicating that surface area is also a factor. This is further supported by our findings that the increased coke yield occurs only with surface-active materials such as Fuller's earth and molecular sieves, whereas it does not so with a material such as glass powder which exhibits no surface activity. Surface area alone cannot, however, offer a complete explanation. The fact that the sharp increase can be obtained only

after pitch: aggregate mixtures have been given a preheating treatment should also be taken into consideration. Preheating probably permits pitch to displace the air or other gases absorbed by the aggregate and to enter into better contact with the latter before being coked. When coking is carried out without preheating, any gases escaping from the aggregate surface presumably interfere with the interaction between the two components. Other factors are undoubtedly involved and consequently no full explanation can yet be offered for the increase in pitch coke yield when binder and petroleum coke are mixed and heated under controlled conditions.

The technique described above provides an additional test for comparison of binders from different sources or of different types; TABLE 1 lists some results obtained and shows that saturation point tends to vary with quinoline insoluble content, but cannot be related to softening point or coking value. The procedure can also be applied to comparison of aggregate cokes, and in certain cases to estimation of binder requirements.

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Aluminium Laboratories Limited for permission to publish.

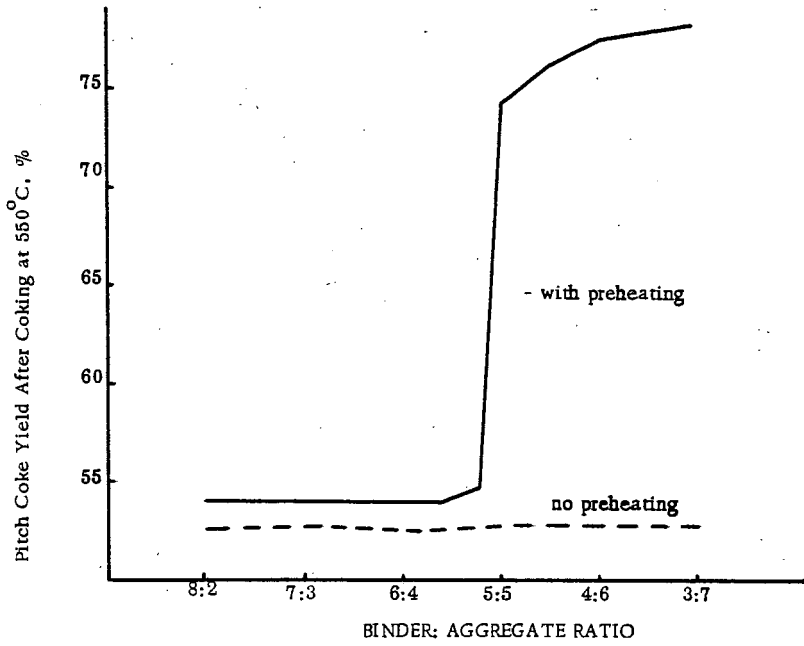


FIGURE 1

EFFECT OF PREHEATING ON PITCH COKE YIELD IN BINDER: AGGREGATE MIXTURE

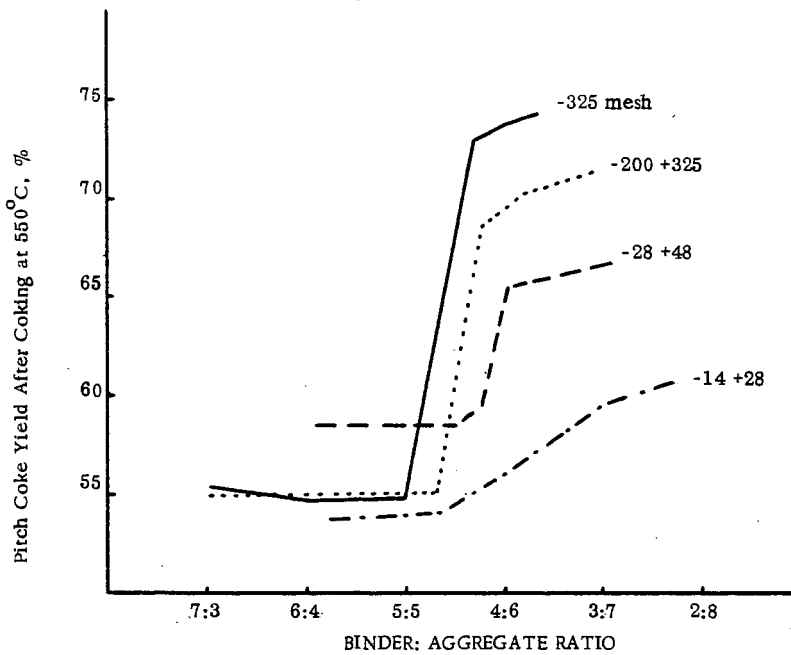


FIGURE 2

EFFECT OF PARTICLE SIZE OF AGGREGATE ON SATURATION POINT AND CURVE

TABLE 1
SATURATION POINTS OF PITCHES FROM VARIOUS SOURCES

Source ^(a)	Pitch ^(b) Type	% Pitch at Saturation Point	Softening Point Cube-in-Air, °C	Coking ^(c) Value %	Quinoline Insoluble %
A	CTP	75	100	62	29
		69	137	65	24
		57	111	62	14
		57	99	55	12
		53	102	53	4
B	CTP	57	50	45	13
		54	113	58	5
		53	112	55	5
		53	87	52	8
C	CTP	57	109	58	11
		53	107	56	8
D	CTP	59	109	57	11
E	CTP	57	92	57	13
F	PP	54	109	54	3
		49	114	56	2
G	PP	50	113	54	0
<p>(a) Letters represent different pitch producers.</p> <p>(b) CTP = coal-tar pitch PP = petroleum-base pitch</p> <p>(c) By regular coking value method. Ref. Fuel, XXXVII, 362-392 (1958)</p>					

Pipeline Gas from Oil Shale by Direct Hydrogasification
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INTRODUCTION

The gas industry has been studying methods for the production of natural gas substitutes from coal and petroleum oils. Processes for direct conversion of these fossil fuels to high heating value gases consisting largely of methane are in an advanced stage of development (6,7). In the case of oil shale, existing technology would involve a preliminary retorting step to produce crude shale oil, and refining to prepare a suitable feed for continuous destructive hydrogenation (hydrogasification). It was reasoned that a direct oil shale hydrogasification process might be preferable because of potentially higher conversion of the organic matter to gas, and elimination of a number of process steps.

Feasibility was shown for direct hydrogasification of the organic matter in Green River oil shale. High heating value gases were produced (1,9,13) in batch reactor tests at 1300°F. at 1200 to 5500 p.s.i.g., and with 100% of the stoichiometric hydrogen requirement for complete conversion of the organic matter to methane. About 90% or more of the organic carbon plus hydrogen content of the oil shale was converted to methane and ethane.

In these tests, the path of the hydrogenolysis of kerogen was only partially indicated at the long heatup times and long gas residence times encountered in the batch reactor. Only the slower final breakdown of higher gaseous paraffins to methane and ethane could be observed. It was also not possible to measure overall reaction rates and precisely determine the effects of temperature. Pressure effects were obscured by changes with temperature and degree of conversion.

The present work was conducted in a reactor system in which oil shale heatup times and exit gas holdup times in the heated portion of the reactor were of the order of a few seconds. After leaving the reactor, the reaction products were cooled rapidly to minimize further reactions.

Three separate test series were conducted. The first test series consisted of semiflow tests with short gas residence times. The purpose of these tests was to measure the rate of kerogen conversion to gaseous products and the rate of mineral carbonate decomposition. The second test series was conducted with a bed of inerts downstream of the oil shale charge, to simulate hot-spent oil shale in a cocurrent flow reactor and to provide time for secondary vapor-phase hydrogenolysis reactions. Here, the overall space velocity which gave methane and ethane as the major products was determined. The third test series consisted of simulated continuous feeding tests to measure the average instantaneous rates of production of gaseous hydrocarbons at controlled hydrogen-to-oil-shale feed ratios.

EXPERIMENTAL

Apparatus

A schematic diagram of the semiflow reactor system is shown in Figure 1. The reactor contained a self-sealing, modified Bridgman closure at each end and was 2 inches in inside diameter, 4 inches in outside diameter, and 60 inches in inside length. The reactor barrel, constructed of Uniloy N-155 super alloy, was rated for operation at a maximum temperature of 1700°F. at 1500 p.s.i.g. The closures were

rated for a maximum temperature of 1400°F. at 1500 p.s.i.g. Satisfactory closure operation was obtained with both 16-25-6 and Inconel-X seal rings. A boundary lubricant of molybdenum disulfide, applied in aerosol form, was used on all closure threads and on the seal rings to prevent galling. This reactor has been completely described elsewhere(11) along with design details which describe the use of externally heated reactors at combined high temperatures and high pressures.

An Inconel-X thermowell of 3/8-inch outside diameter, with a 12-gage wall thickness and 58 inches long, was mounted axially in the bottom closure. The thermowell could contain up to five 0.040-inch outside diameter thermocouples. Thermocouples were chromel-alumel, magnesium oxide insulated, and enclosed in a swaged Inconel sheath. To provide for complete containment and recovery of the oil shale residue, the reactor was provided with a removable stainless steel insert, 1-5/8 inches in inside diameter by 1.990 inches in outside diameter and containing a 1/2-inch outside diameter thermowell sleeve.

The reactor was heated by means of an electric resistance furnace containing four separately controlled heating zones, consisting of four rectangular heating elements, 7 inches wide and 12 inches long. Temperatures were controlled manually during tests but were controlled by pyrometric controllers during reactor heatup. Each temperature was recorded at approximately 3-second intervals by means of a high-speed potentiometric temperature recorder during the test period.

A feed hopper was mounted directly above the reactor and was provided with a vibrator to aid oil shale feeding. A full-opening, air-operated ball valve was installed between the hopper and the reactor. A second hopper contained a rotating-drum type feeder, which was driven by a variable speed drive, for continuous oil shale feeding.

Feed hydrogen flow rates were controlled manually and were measured by means of an orifice meter. The orifice pressure and the reactor pressure were recorded continuously. The feed hydrogen was preheated to reaction temperature within the reactor. Exit gases passed through a water-cooled coil, a liquids knockout pot, a high-pressure filter and a pressure-reducing back-pressure regulator, before being sampled, metered and monitored. A sampling manifold was installed upstream of the metering and monitoring system. The exit gas specific gravity was monitored by means of a recording gravitometer.

Materials

In all tests, the feed hydrogen contained an accurately measured small amount of helium, usually 1-2 mole %, as a tracer for exit gas flow rate measurement. The gases were mixed during compression and stored in high-pressure cylinders at pressures up to 3000 p.s.i.g. Commercially available grades of electrolytic hydrogen (99.8% pure) and helium (99.99% pure) were used. The oil shale used in all semiflow tests was supplied by the Union Oil Company. An analysis of the oil shale is given in Table I.

Procedure

The semiflow experimental technique employed in the majority of the tests followed closely that employed in coal hydrogenolysis studies described recently (2,11). Most tests were of 15-minute duration or less. After the reactor was heated to the desired operating temperature, the unit was pressurized and gas flow was

started. Heat inputs were then adjusted until all recorded reactor temperatures remained constant. When flow rates, temperatures, and pressures had been stabilized completely, the feed gas was sampled. Tests were initiated by opening the quick-opening ball valve connecting the hopper and the reactor. The vibrator mounted on the hopper was started only a few seconds before the start of the run to avoid compacting the oil shale charge.

The feed gas orifice calibration was checked before each run with a wet test meter. Exit gases were also metered with the wet test meter during each test, as a check on the flow rates calculated using the helium tracer. The exit gas specific gravity record was used as an aid in selecting times for exit gas sampling; in tests conducted to simulate continuous operation, it was also used to check the length of the oil shale feeding period, since it was not always possible to obtain positive proof of the initiation of solids feeding. Gas analyses were performed by mass spectrometer. Except for the last three tests conducted in the series to simulate continuous operation, combined values for nitrogen plus carbon monoxide are reported, because of the inability to distinguish precisely between these two gases by the mass spectrometer. In the last three tests, carbon monoxide was also determined by infrared spectrophotometer and nitrogen was obtained by difference.

In the first series of tests, single charges of oil shale weighing from 10 to 200 grams were fed. These charges were allowed to fall freely from the hopper, which resulted in a charging rate of about 7 grams per second. Small amounts of high-purity alumina inerts, up to 4 inches in depth, were placed in the reactor before the run to support the shale charge and to position it in the center of the third reactor heating zone. Temperatures were recorded for thermocouples located at the center of the oil shale charge and at a point 6 inches above the charge to show whether the feed hydrogen was being preheated completely before reaching the charge.

Table I.-ANALYSIS OF COLORADO OIL SHALE

Sample Designation	4770
Type	Colorado, Mahogany Zone
Source	Union Oil Company
Particle Size, U.S. Standard Sieve	-8,+20
Analysis, wt. % (dry basis)	
Moisture	0.3 ^d
Organic Carbon ^a	17.45
Mineral Carbon ^b	4.84
Hydrogen ^a	2.36
Organic C/H Wt. Ratio	7.4
Fischer Assay Oil, gal./ton ^c dry shale	35.9
a. ASTM method D271-58 adapted in accordance with technique of Grace and Gauger (3).	
b. Method A-3, U. S. Bureau of Mines.	
c. Modified method of Stanfield and Frost (14).	
d. On oven-dry basis (dried for 1 hr. at 105°- 110°C.).	

Since the void volume in the bed of inerts was small, exit gas holdup times in the system downstream of the reaction zone were small. At typical operating conditions of 1300°F., 1000 p.s.i.g., and 100 SCF per hr. feed hydrogen flow rate, the total exit gas holdup time was only about 10 seconds, based on the appearance of the first hydrogasification products in the exit gas sample. Gas residence times in the reactor proper at these conditions were less than 5 seconds. During the initial period of high rate of hydrogasification, gas samples were taken at intervals as short as 5 seconds and thereafter at time intervals sufficiently small to delineate the entire course of the reaction. The last gas sample was usually taken at 480 seconds, at which time its methane content was less than 0.1 mole %.

The second series of tests was conducted with larger amounts of alumina inerts below the oil shale bed to provide sufficient residence time for the primary reaction products to undergo further hydrogasification after leaving the reaction zone. Sufficient alumina inerts, to simulate spent shale, were placed in the reactor prior to each test to give a total bed volume (oil shale plus inerts) of 0.02 cu. ft. Since gas flow rates were varied from 10 to 200 SCF per hr., the feed hydrogen space velocity varied from 500 to 10,000 SCF per cu. ft. bed-hr., and exit gas holdup times ranged from about 200 to about 10 seconds, respectively. Temperatures of the center of the inerts and of the bottom of the oil shale charge were recorded. Here, as in earlier tests, gas samples were taken at those time intervals required to delineate the entire course of the reaction.

In the third series of tests, continuous operation was simulated by semicontinuous feeding of oil shale. In the first few tests, oil shale was fed by opening the ball valve, connecting the reactor and feed hopper, every 15 or 20 seconds for 1 second and for total charging times of from 465 to 840 seconds. In later tests, conducted with a rotating drum-type feeder, oil shale feed rates were about 5.5 pounds per hour. Approximately 0.01 cu. ft. of alumina inerts was placed in the reactor prior to each of these tests to minimize changes in feed hydrogen space velocity accompanying bed volume changes, and to provide a zone simulating a bed of spent oil shale wherein primary reaction products could be further reacted. This resulted in a total bed volume (oil shale plus inerts) which increased to a final value averaging about 0.02 cu. ft. Since, in these tests, the inlet hydrogen-to-oil-shale ratio was varied by varying gas flow rates, the exit gas holdup times also varied. Temperatures of the bottom of the oil shale bed, of the bottom of the inerts, and of the center of the final oil shale bed were recorded. Gas samples were taken during and after the feeding period.

Exploratory Tests

Exploratory tests to select the proper combinations of oil shale sample weights and feed hydrogen flow rates were made at 1300°F. and 1000 p.s.i.g.

To approach isothermal as well as differential reactor conditions, it was necessary that the smallest oil shale sample weights be used for a given feed gas flow rate which still permitted accurate product analysis. However, it was also necessary to maintain a sufficient sample size so that representative samples of the highly heterogeneous feed could be prepared by riffing of larger batches.

Feed gas flow rates were set as high as possible to keep the residence time of the reaction products in the exit gas system small so as to minimize secondary vapor phase reactions. This also minimized backmixing of reaction products in the exit gas system and oil shale particle heatup times. A feed hydrogen flow rate of 100 SCF per hour was calculated to be the minimum gas flow rate which could be used, assuming complete mixing in the exit gas system, without distorting the true relationship between reaction rate and time.

With 50- and 25-gram samples, the maximum exit gas hydrocarbon concentration was too high at this hydrogen feed rate, and temperatures changed too greatly to allow the assumption of differential and isothermal reaction conditions. In tests with 10-gram samples, exit gas hydrocarbon concentrations and reaction zone temperature changes approached practical limiting values. With such small samples, however, quantitative recovery of liquids was not possible.

The observed rates of conversion may have been largely a function of heat transfer. The lack of accurate thermophysical data for oil shales makes calculation of particle temperatures difficult. However, heat transfer calculations indicated that the -8, +20 U.S.S. size oil shale particles would be preheated to at least 1100°F. in falling from the hopper through the top two reactor heating zones.

As shown in Figure 2, there were large increases in the specific rate of conversion, expressed as pounds of carbon as gaseous aliphatic hydrocarbons formed per pound of organic carbon fed per hour, with decreases in sample weight. Therefore, to obtain differential rates of reaction, it was necessary to prepare a cross-plot of reaction rates versus sample weight at selected levels of organic carbon conversion. By plotting on semilogarithmic coordinates (logarithm of reaction rate versus sample weight) a family of curves was obtained for the parameter, percent conversion. These curves approached straight lines as sample weights approached zero so that reasonably good rate values for zero sample weight could be obtained by linear extrapolation. Reaction rates obtained by this cross-plotting technique are shown in Figure 3, as a function of conversion.

RESULTS

Single-Charge Tests at Short Gaseous Product Residence Times

A series of tests was conducted at temperatures of 1100°, 1200°, 1300° and 1400°F. to measure the effect of temperature and conversion on gaseous aliphatic hydrocarbons on the rate of conversion of organic carbon (Figure 4). These results show a large increase in rate with increases in temperature. The effects of increases in temperature and hydrogen flow rate on gaseous and total product distribution are shown in Figures 5 and 6. The gaseous aliphatic hydrocarbon yields, and the percentage of paraffins, increased with increases in temperature and decreased with increases in feed hydrogen flow rate. The variation of liquid yields was the opposite of gas yields. These results indicate that the major steps in the hydrogenolysis of kerogen are:

- 1) Kerogen decomposition with initial formation of intermediates at least partially recoverable as liquids at very short residence times and/or low temperatures.

- 2) Pyrolysis, hydrogenation and hydrogenolysis reactions leading to gaseous aliphatic hydrocarbons of decreasing molecular weight and, finally, ethane and methane, along with some aromatic liquids.

A comparison of the gaseous molecular hydrogen consumption with the elemental gaseous hydrogen balance is given in Figure 7. At low levels of organic carbon conversion to gaseous aliphatic hydrocarbons, the amount of hydrogen donated by the oil shale is approximately equal to the amount of feed hydrogen consumed. Thus, pyrolysis and hydrogenation reactions probably occur simultaneously. At high conversion levels, no accurate measurement can be made.

Rates of carbonate decomposition were also measured, although separate infrared spectrophotometer analyses were not performed for carbon monoxide. Mass spectrometer analyses indicated, however, that nitrogen was negligible in comparison to carbon oxides. The strong increase in decomposition rate with increase in temperature is shown graphically in Figure 8. These rates are much higher than those measured by Jukkola and others (4) in nitrogen or carbon dioxide at 1 atmosphere. This may be due to the more rapid oil shale heatup and the lower concentration of carbon dioxide in these tests. The large increase in decomposition rate between 1200°F. and 1300°F. is probably due to the combined decomposition of both magnesium carbonate and calcium carbonate above 1200°F. Jukkola and others (4) found that calcite in oil shale begins to dissociate at 1150° to 1250°F. Since the molar ratio of calcium carbonate to magnesium carbonate is 2.3 in this oil shale any rate differences in a transition from a region where only magnesium carbonate decomposes at a measurable rate to one where both carbonates decompose measurably fast would be accentuated. It would be desirable to minimize mineral carbonate decomposition in large-scale processing since the decomposition reactions are endothermic and part of the feed hydrogen is consumed by reaction with part of the carbon dioxide formed. Equilibrium carbon dioxide partial pressures for magnesium and calcium carbonate breakdown, shown in Figure 9, indicate that it might be feasible to inhibit calcium carbonate decomposition, but not magnesium carbonate decomposition, by maintaining a high carbon dioxide partial pressure.

Single-Charge Tests at Long Product Residence Times

There were several shortcomings in the above tests. First, product residence times were short and liquid and olefinic gaseous hydrocarbons were major products. Second, product residence times in the reactor could not be practically controlled since they were a function of many other variables (e.g., temperature, pressure, flow rate and oil shale sample size). For process design purposes, it is necessary to show the effects of variables under conditions where gaseous paraffins are the primary products.

Therefore, the test program was supplemented by tests using a bed of inerts downstream from the oil shale bed to simulate spent oil shale in a practical reactor system, which would allow further conversion of higher molecular weight hydrocarbons to gaseous paraffins. As can be seen in Figure 10, the above objective was met in these tests. The fraction of gaseous hydrocarbon carbon appearing as methane plus ethane was about 80 % or more over the entire range of space velocities employed. In addition, only about 2% or less of the gaseous hydrocarbon carbon was nonparaffinic.

The results shown in Figure 10 are consistent with the reaction sequence described earlier. At the lower feed hydrogen space velocities, the conversion to gaseous hydrocarbons was reduced by coke formation due to the lack of sufficient hydrogen. At the higher feed hydrogen space velocities, the conversion to gaseous hydrocarbons reached a nearly constant value. The slight decrease at the highest feed hydrogen space velocities was accompanied by an increase in liquids, which indicates that products residence times were insufficient for conversion of liquid intermediates to gaseous hydrocarbons. The apparent increase in the maximum rate of conversion to gaseous hydrocarbons with increases in feed hydrogen space velocity above 5000 SCF/cu. ft.-hr. was primarily the result of increased linear velocity of the rapidly formed intermediate reaction products. Backmixing effects were found to be negligible over most of the range of flow rates studied (5).

Simulated Continuous Tests

In view of the important effect of the hydrogen-to-oil-shale feed ratio on product distribution, the semiflow techniques were modified to permit control of this variable. Initially, small batches of oil shale were fed at frequent intervals onto a fixed bed of inerts. Results still showed an apparent effect of feed ratio above 100% of the stoichiometric requirements for conversion of the organic matter to methane, which was unexpected on the basis of oil hydrogasification results (8,10,12). However, these tests showed the expected negligible effect of an increase in total pressure from 1000 to 2000 p.s.i.g.

Further tests at 1200° to 1400°F. and 1000 p.s.i.g. were then conducted with a continuous feeding system in which oil shale was charged at a nearly constant rate for 510 seconds, corresponding to an average oil shale residence time of about 5 minutes. Thus, the hydrogen flow rate increased linearly with hydrogen-to-oil-shale ratio. As shown in Figure 11, instantaneous organic carbon gasification at hydrogen-to-oil-shale feed ratios ranging from about 100 to 250% of stoichiometric remained nearly constant and averaged 63 to 64%. Total organic carbon gasification measured during the 1000-1100 second run period was about 70%. The organic carbon distribution in the residue and the aromatic liquid products was about 13% each, at the lowest gas rate. The organic carbon in the residue decreased with an increase in hydrogen feed rate, as would be expected. All yield and organic carbon distribution data are uncorrected for low carbon balances (92 to 96%).

Higher conversions to gaseous hydrocarbons could, of course, be obtained by increasing oil shale residence times, although the maximum would be about 85 to 90% since a minimum yield of aromatic liquids of 10 to 15% would be expected from previous experience in hydrogasification of petroleum hydrocarbons similar in composition to kerosene (8,10,12).

ACKNOWLEDGMENT

This work was supported by the Gas Operations Research Committee of the American Gas Association with funds provided by the Promotion-Advertising-Research Plan of the Association. The guidance and counsel of the Project Supervising Committee under the chairmanship of C. F. Mengers were very helpful. Thanks are due to E. B. Shultz, Jr., who designed most of the equipment and helped develop much of the experimental procedure. F. C. Rac, N. Mechaes, A. E. Richter and R. F. Johnson assisted in conducting tests. D. M. Mason and J. E. Neuzil supervised the analytical work.

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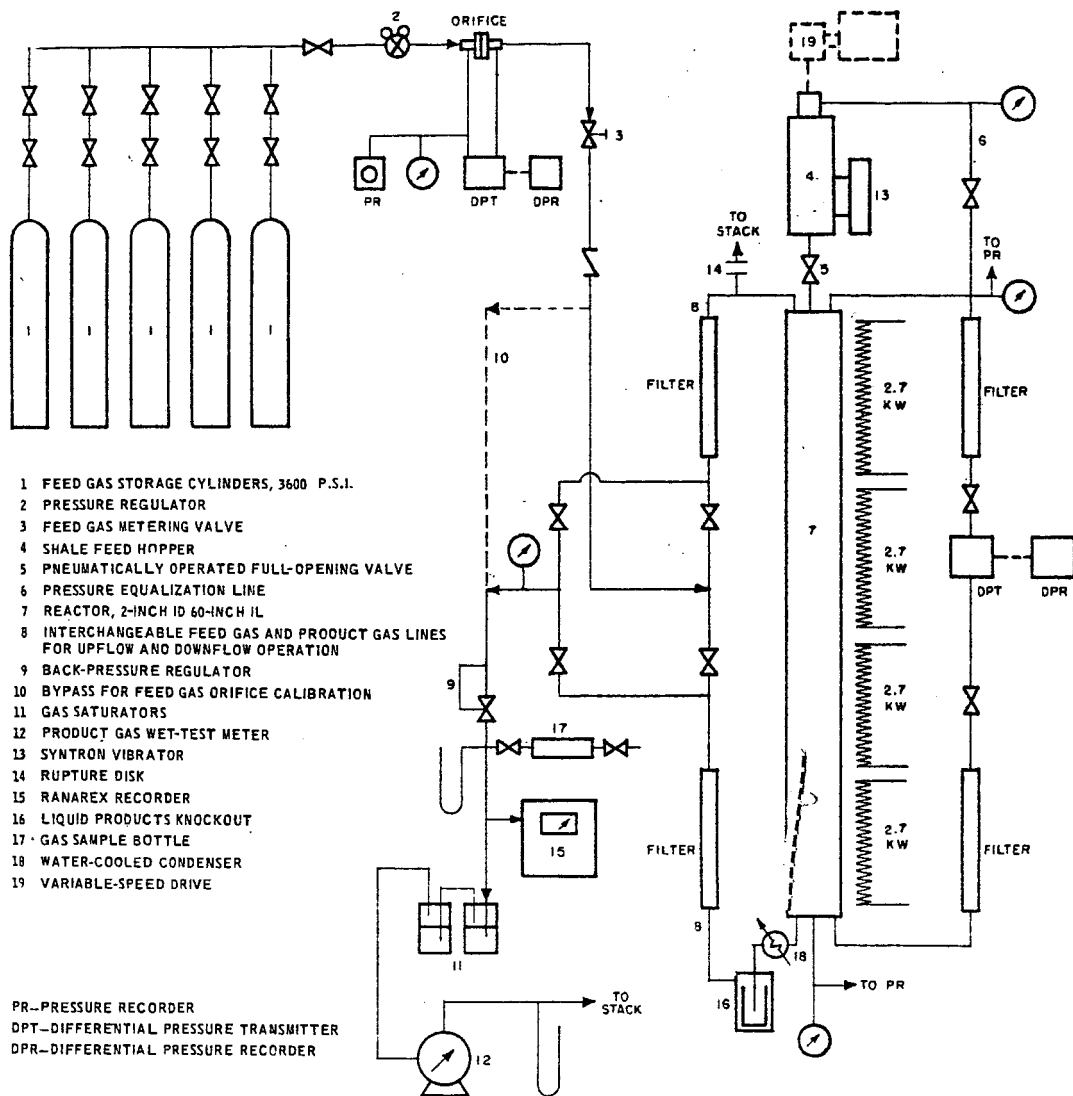


Fig. 1. Semiflow Reactor System for Study of Rates of Hydrogasification of Oil Shale at Temperatures to 1700° F and Pressures to 3000 p.s.i.g.

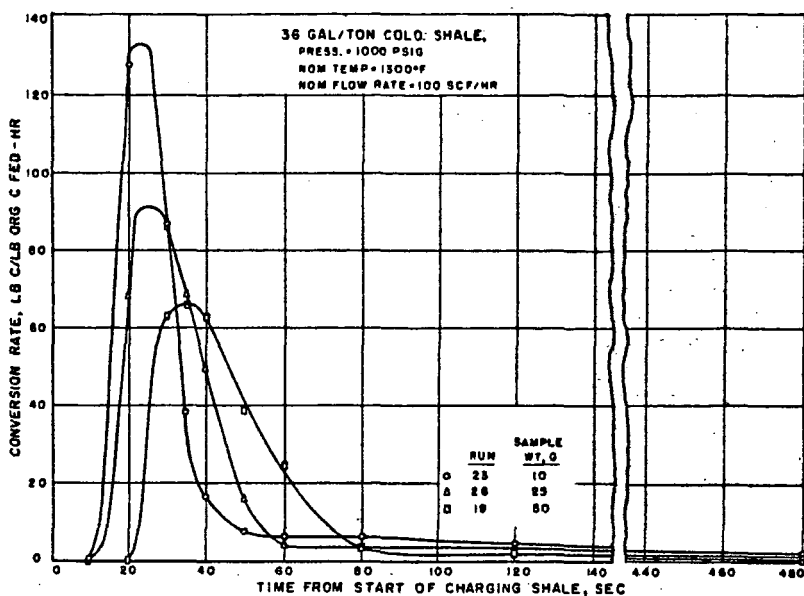


Fig. 2.-Effects of Sample Weight and Time on Rate of Conversion of Organic Carbon in Oil Shale to Gaseous Aliphatic Hydrocarbons

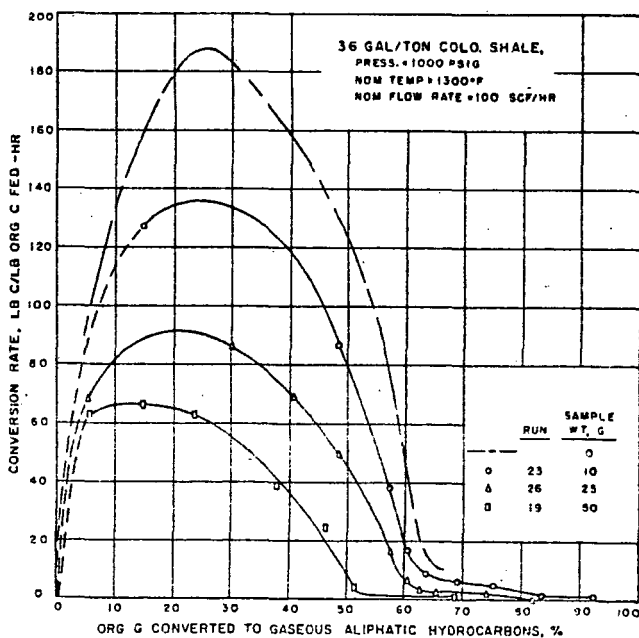


Fig. 3.-Effects of Oil Shale Sample Weight and Organic Carbon Converted to Gaseous Aliphatic Hydrocarbons on Conversion Rate

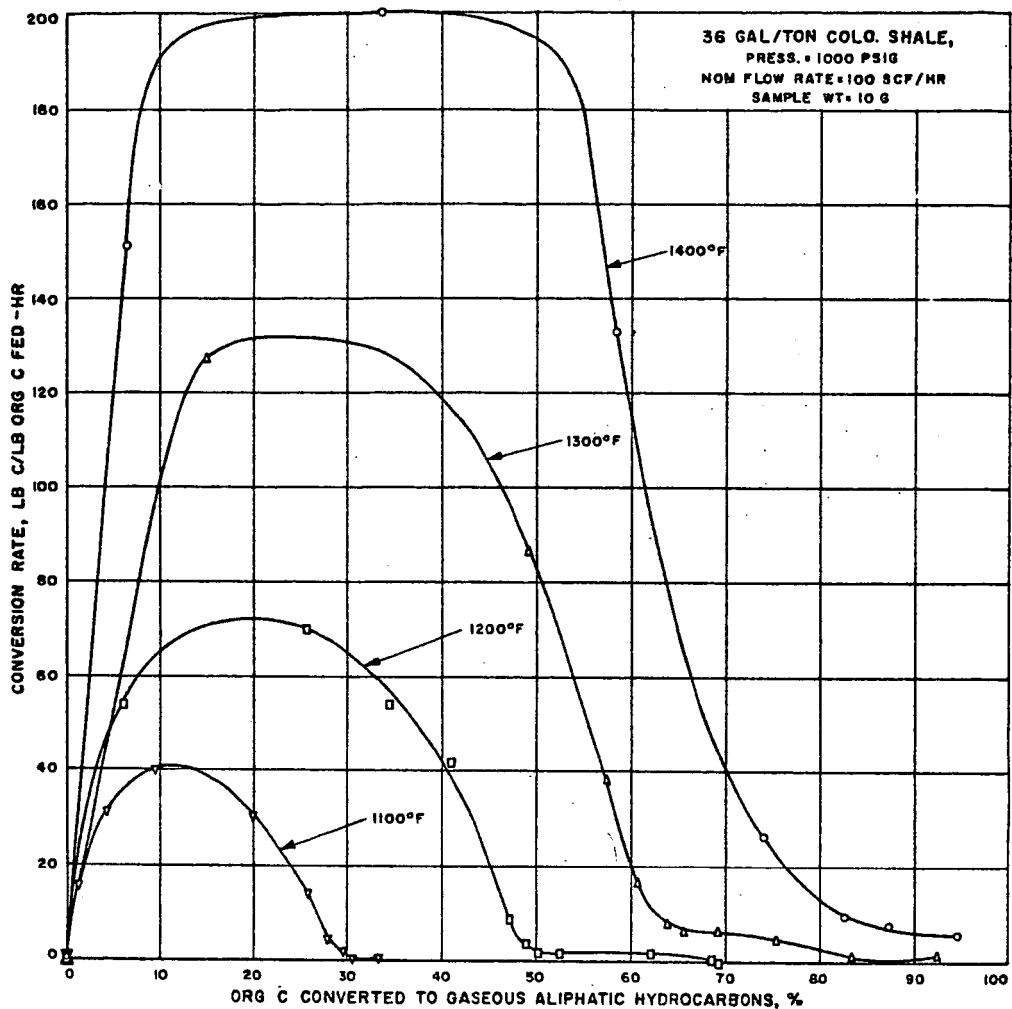


Fig. 4.-Effects of Temperature and Organic Carbon Conversion to Gaseous Aliphatic Hydrocarbons on Conversion Rate

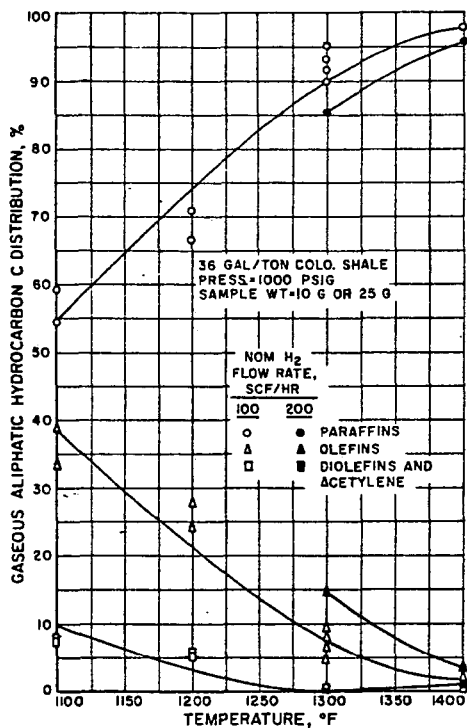


Fig. 5.-Effects of Temperature and Feed Hydrogen Flow Rate on Average Gaseous Aliphatic Hydrocarbon Distribution During First Minute of Gasification

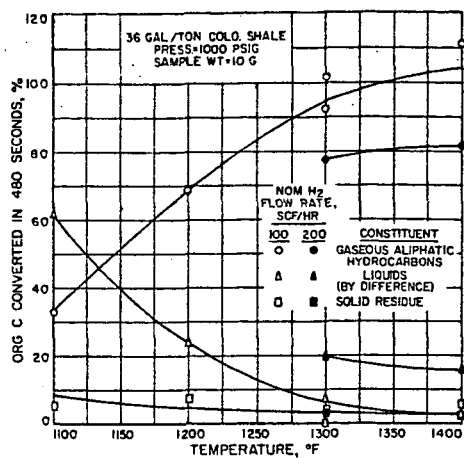


Fig. 6.-Effects of Temperature and Feed Hydrogen Flow Rate on Conversion of Organic Carbon to Gaseous Aliphatic Hydrocarbons, Liquids and Solid Residue

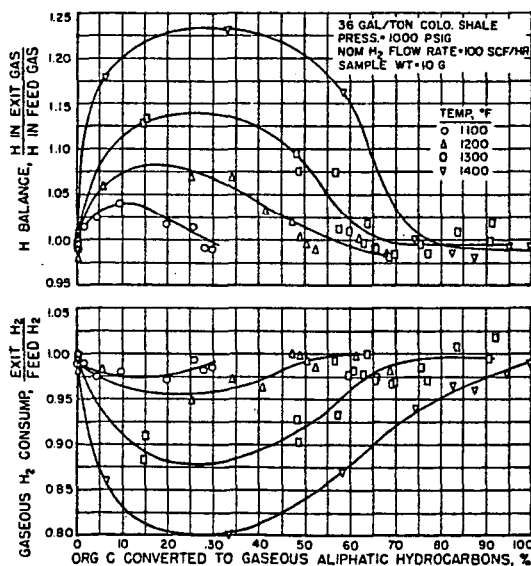


Fig. 7.-Gaseous Hydrogen Balances as a Function of Temperature and Organic Carbon Conversion

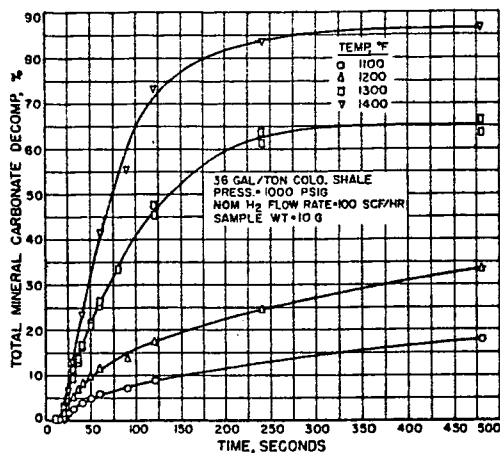


Fig. 8.-Effects of Temperature and Time on Mineral Carbonate Decomposition

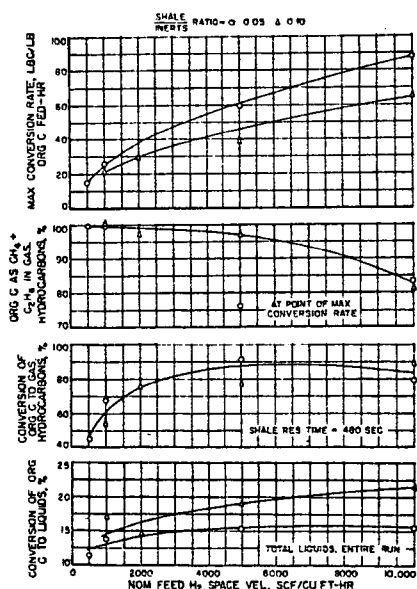


Fig. 10.-Effect of Feed Hydrogen Space Velocity on Organic Carbon Converted to Liquids and Ethane Plus Methane and on the Maximum Conversion Rate

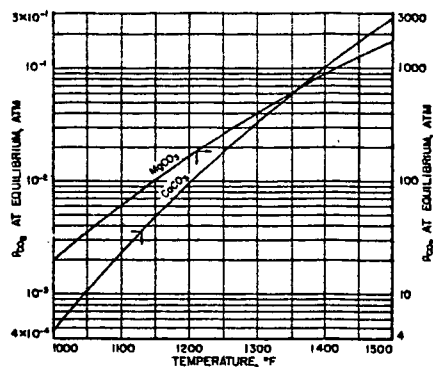


Fig. 9.-Effect of Temperature on Equilibrium Carbon Dioxide Partial Pressures for Magnesium Carbonate and Calcium Carbonate Decomposition

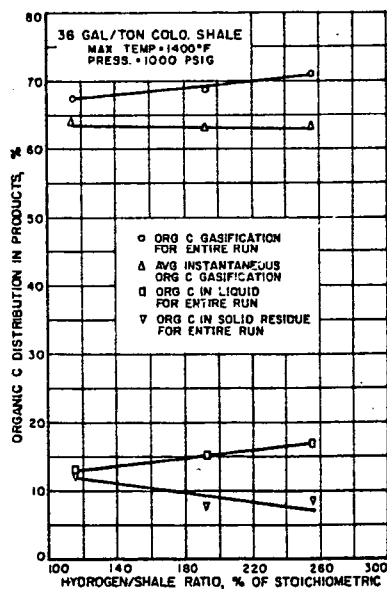


Fig. 11.-Effect of Hydrogen/Shale Ratio on Carbon Distribution in Products and Average Instantaneous Carbon Gasification

Chemical Structure of Bituminous Coal

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Introduction

The purpose of this paper is to survey present knowledge of the structure of coals in such a way as to provide a useful background to consideration of the production of chemical by-products. In addition some deductions will be drawn from structural knowledge about the probable contribution made by different coal components and by different parts of the structure to the volatile matter evolved on carbonization. Since the survey has only this limited objective, no attempt will be made to treat the subject exhaustively; and since detailed, fully documented, reviews have appeared recently^{1,2}, a full bibliography is not provided.

Examination of a sample of coal with the naked eye or under the microscope reveals that the material is apparently heterogeneous. There are bands of different reflectance running through the coal, and even minute areas scanned microscopically show a variation of optical properties; moreover, there are regions showing various types of fossilized plant remains. These components have been classified in various ways, and there is no universally agreed system; moreover, the subject is complex since a large number of alleged components have been distinguished. The term "alleged" is used in recognition of the fact that the significance of a component can only be established to the satisfaction of coal scientists at large if it has been separated physically and shown to differ appreciably in chemical and physical properties and in carbonization behavior from material associated with it in the whole coal. The real significance of many components has not yet been established in this way.

For present purposes it will be sufficient to postulate that bituminous coals are composed of three major "maceral" groups, which, in the common European terminology are known as vitrinite, exinite and inertinite. The term "inertinite" refers to components inert in carbonization; "inert" does not imply that the materials undergo no chemical reaction, only that they do not soften or swell on heating and contribute little to the volatile matter. Vitrinite is quantitatively the most important maceral, accounting for probably 60-80% of most worked coals, and it is the material primarily responsible for the characteristic coking behavior of higher rank bituminous coals. Coals relatively rich in the other components are known, but they are rare in the U.S.A.; nevertheless, even in minor amount, they can make significant contributions to the properties of the whole coal.

In what follows, the structure of vitrinites will be considered first. So far as possible the conclusions stated will be based on work with pure macerals, but some evidence relative to vitrains (bright bands of coal seams, normally containing 80-95% vitrinite) will be used where it seems improbable that the character of broad qualitative conclusions could be altered by the presence of small amounts of petrographic impurity. After the consideration of vitrinites, available evidence on structural differences between them and other macerals will be reviewed; at this point some comments will be made on the sub-components of the main maceral groups.

The Structure of Vitrinites

It has long been believed that vitrainous coals are predominantly aromatic in structure. The partly aromatic nature of coals is established qualitatively by the presence of certain bands in their infra-red spectra. However, the fullest

and most convincing evidence on this point comes from the study of the scattering of x-rays by coals. The interpretation of the scattering data is a difficult and complex business, and no completely adequate treatment has yet been devised. The method most recently published³ makes use of a curve-fitting procedure, in which the scattering curve calculated for various hypothetical models is compared with the curve observed experimentally. Of the models tested, the one that gave the best fit required the supposition that in bituminous vitrinites a majority of the carbon was organized into aromatic nuclei containing on the average 2-3 fused rings. For reasons that need not be discussed here the published work does not permit any accurate estimate of the fraction of carbon atoms in such systems nor any information about the other carbon atoms. The indications from the x-ray work, and the study of infra-red spectra, are that the aromaticity is between about 60 and 85%, increasing with rank, though lesser figures are possible. Further work may alter this estimate but is unlikely to change much the sizes of the nuclei quoted above.

In view of its obvious importance, much ingenuity has been expended in trying to devise methods of calculating the aromaticity from such physical properties as density and refractive index by "physical constitution analysis". For what they are worth, the results are in accord with the figures just given.

Non-aromatic carbon must be presumed aliphatic, and indeed the infra-red spectra of vitrinites demonstrate that aliphatic material is present. J. K. Brown⁴ was able to estimate the ratio of aromatic to aliphatic hydrogen in a series of vitrains from the spectra, and his values have recently been confirmed (with a small revision towards higher values) by nuclear magnetic resonance studies^{5,6}. It appears that vitrains of carbon content between 80 and 90% have the ratio H_{ar}/H_{al} rising from about 0.20 to 0.50, that is between 80 and 50% of the hydrogen is attached to aliphatic carbon atoms. The proportion of hydrogen in methyl groups cannot be measured by infra-red methods, but the relative intensity of the methyl vibration at 1375 cm^{-1} indicates that these groups are rare compared with CH_2 . N.m.r. data confirm this⁶, and indicate a fair proportion of tertiary $\rightarrow\text{CH}$. The spectra show that in the lower rank coals, the aromatic nuclei are highly substituted.

Many workers have studied phenolic hydroxyl in coals, by a variety of methods (see refs. 1, 2 for a review). It is established that between 40 and 80% of the oxygen in bituminous vitrinites is present at this type of functional group.⁷ Most of the balance of the oxygen is in some form of strongly conjugated carbonyl.

Several groups of workers have investigated the dehydrogenation of hydroaromatic structures in coals, and it is now certain that much of the aliphatic hydrogen is attached to such structures rather than to alkyl groups or other forms of alicyclic rings^{9,10}. The proportion of hydrogen removeable by two different dehydrogenation reactions falls from about 30-40% at a carbon content of 82-84% to 12-25% at 89-90% C. These figures correspond to minimum fractions of carbon in hydroaromatic rings in the region of 30 and 12% respectively. These data, together with n.m.r. and infra-red spectroscopic results, indicate that in the average composition of the aliphatic part of coals, CH_n , n is considerably less than 2, at least for the lower rank materials. This implies, though does not prove, that very little hydrogen or carbon can be present in alkyl groups or non-hydroaromatic alicyclic rings (it should be recalled that there is no evidence of the presence of olefinic or acetylenic groups in coals, which could also lead to a low value of n).

The molecular weights of coals are not known; determinations with solvent extracts² give values between about 500 and 3000. Therefore each molecule must contain a number of aromatic nuclei, linked together by non-aromatic groups. Attempts to make a synthesis of all the above information^{9,10} show that it is difficult or impossible to suggest any type of molecular structure that does not employ the hydro-aromatic carbon as a means of linking the aromatic nuclei. The most obvious expression of this principle is the 1,2- and 1,4-cyclohexadiene ring present in the 9,10-dihydro-

phenanthrene and -anthracene molecules respectively, where two benzene rings are linked by two methylene groups which complete a third, non-aromatic, ring. Other possibilities have been discussed². The "depolymerization" experiments of Heredy and Neuworth¹¹ also strongly suggest that the aromatic nuclei are linked together by methylene bridges, though here there is no necessary implication that these constitute hydroaromatic rings.

We have therefore arrived at the following picture of the structure of bituminous vitrinites. Each molecule contains a number of aromatic nuclei containing from 1 to 5 or 6 fused rings, the majority containing 1, 2 or 3 rings. Each aromatic nucleus contains few replaceable hydrogen atoms. The substituents are partly phenolic hydroxyl and carbonyl oxygen, and partly aliphatic carbon atoms that are disposed in such a way as to constitute hydroaromatic rings and to serve as linkages connecting the aromatic nuclei together. In addition there is a minor proportion of short alkyl chains and perhaps non-hydroaromatic alicyclic rings (the latter includes the cyclopentadiene ring system as found in indene and fluorene). Such molecules would be very markedly non-planar. As an illustration of what is meant by this description, Fig. 1 shows a segment of a hypothetical coal molecule.

It should be noted that on this view each coal molecule is a true statistical sample of the bulk material, in the sense that each contains all the known structural features in approximately the same proportions. The older view of coal structure as a kind of strawberry jam, containing lumps of graphitic material embedded in a continuous medium, the bitumen, therefore becomes meaningless. Furthermore, in the model proposed the aliphatic and aromatic parts are so intimately integrated in the molecular units that one cannot label one part as tar-forming and another as coke-forming.

Structure of Exinite and Inertinite Materials

The exinite or leptinite suite includes a group of components not derived, like vitrinite and fusinite, from woody tissue. The most abundant member of the group, about which most is known, is sporinite, the remains of plant spores (indeed, the name exinite is often used to mean only this type of material). Sporinite contains considerably more hydrogen, and less oxygen, than the associated vitrinite. It is less soluble in organic solvents, more resistant to oxidation, and has a lower aromaticity (see the excellent review by J. K. Brown¹² and references therein). A group of spore exinites from British coal seams was found to contain more hydroaromatic hydrogen (corresponding to a minimum fraction of hydroaromatic carbon equal to about 0.4) than the associated vitrinites; less phenolic hydroxyl was found, both as a fraction of the weight of coal and as a fraction of the total oxygen¹³. The aromatic nuclei are about the same size as those in vitrinites, but the mean interlayer spacing is larger¹², suggesting that frequent occurrence of naphthenic structures keeps the planes apart¹². It was concluded¹³ that sporinites probably contain the same type of molecular structure as vitrinites, but that the molecules are larger, less polar and more hydroaromatic.

Exinites have a highly characteristic behavior on heating. Of whatever rank, they soften at around 400° and acquire a fluidity much too high to be measured with a Giessler plastometer. Even 60% exinite concentrates have fluidities greater than 20,000 divs per minute¹⁴. They swell enormously to a thin fragile bubble structure, which is so weak that a dilatometer piston sinks and resolidification cannot be observed this way. The loss in weight in the volatile matter test is much greater for exinites than for vitrinites and is in many cases 70-80%.

Little is known of the other members of the leptinite suite. Resinite, the remains of plant resins and waxes, is widely distributed in small amount, and also appears to be hydrogen-rich and very fluid when heated. The other components, cutinite (from cuticles), alginite (found only in boghead coals) and sclerotinite (from fungal sclerotia) are probably of little importance for present purposes.

The inertinite group contains two major components, fusinite and micrinite.

Fusinite closely resembles charcoal; its carbon content is always over 91%,¹¹ it does not show fluidity or swelling, it contributes little to the volatile matter¹², and chemically it is relatively unreactive¹³. Micrinites have appreciably higher carbon and lower hydrogen contents than the associated vitrinites, though the difference is not so extreme as it is with fusinites. The aromatic nuclei are larger than in vitrinites. Both micrinites and fusinites are virtually opaque to infra-red radiation, and so no spectra have been reported. Both macerals undergo substitution with N bromosuccinimide, a reagent specific for placing bromine on aliphatic carbon in the α -position to a double bond (e.g. the methyl groups in propylene or toluene); this suggests that at least some aliphatic material is present^{15,16} (see Table I). Both also contain some phenolic hydroxyl. Micrinites do not swell or become fluid on heating.

For convenient reference some properties of sets of macerals each separated from one seam are collected in Table I. Two German and four British coals are included; no corresponding data have yet been published for American coals so far as the author is aware. Data will be found in the Table that support the statements made above about differences in elemental composition, hydroxyl contents, etc. It will be noticed that the exinites associated with British and German vitrinites of closely similar rank differ considerably in yield of volatile matter.

Unfortunately reflectance data are not available for the samples quoted, and so some refractive indices are included as an indication of optical properties.

Chemical Changes on Heating

Little direct experimental evidence is available on this subject, but available information can be usefully supplemented by the results of experiments on models and by predictions from the type of structure believed to be present.

The phenolic hydroxyl content of bituminous vitrains drops sharply to low values when the coal is heated to 450-500°¹⁸. Preliminary experiments on two vitrains, using Peover's method with benzoquinone, suggest that the hydroaromatic hydrogen content also drops sharply in a similar or somewhat lower temperature range¹⁸. The infra-red spectra of vitrains heated to 400° shows little change, except that the aliphatic C-H and phenolic OH absorption are slightly weaker¹⁹. By 460° aliphatic CH is much weaker, and OH slightly so; the H_{ar}/H_{al} ratios of two vitrains of carbon contents 82 and 89% had reached 2.4 (values for the unheated coals were about 0.25 and 0.6 respectively, and for the higher rank coal heated to 400°, 0.8). By 550° both OH and aliphatic C-H are very weak, but the aromatic C-H bending frequencies at 700-900 cm.⁻¹ are still well-defined. Above this temperature the coals become opaque, owing no doubt to incipient graphitization. No significant changes in x-ray scattering are observed until a vitrain has been heated to 500°, at which temperature the growth of the aromatic nuclei begins to be noticeable²⁰. Between 500 and 1000° there is further continuous growth, the average layer diameter of one sample, for example, increasing from 7Å to 14Å. It will be recalled that the free radical content of vitrain chars²¹ passes through a sharp maximum at 500-550°, the maximum rate of volatile evolution occurs at about 450°, and electrical conductivity increases sharply (by many orders of magnitude) in the range 600-650°²².

Dryden and his co-workers have studied the primary products of the evolution of volatile matter from vitrains by two methods: (a) study of the chloroform-soluble material extractable from coals heated very rapidly to temperatures near 400°; (b) distillation or pyrolysis of coals spread in thin layers on a heated plate in a high vacuum, a condenser being placed just above the plate. They find the extract and distillate to have closely similar infra-red spectra, and to resemble the original coal spectroscopically much more closely than a tar. These materials appear to play an important part in producing fluidity and resolidification to a coke when a coking coal is carbonized. They conclude that the materials mostly exist as such in the raw coal and are only to a small extent products of decomposition. However,

Table I. Properties of Macerals separated from British and German Coals.

Colliery and Seam Source of data, ref.	Markham Main, Barnsley 13, 14, 15			Dinnington Main, Barnsley 13, 14, 15			Zollverein 12, 17			Aldwarke Main, Silkstone 13, 14, 15			Chislet, No. 5 13, 14, 15			Anna 12, 17		
	V	E	F	V	E	F	V	E	M	V	E	F	V	E	F	V	E	M
%C, d.a.f.	82.3	81.6	91.6	85.1	84.3	92.4	85.7	87.4	88.0	86.9	87.1	92.1	88.6	89.1	92.2	88.4	89.1	89.6
H	5.5	7.6	3.6	5.3	7.6	3.1	4.9	6.7	4.2	5.4	7.4	3.7	5.3	6.2	3.8	5.1	5.0	4.3
O	9.3	8.4	3.4	6.9	5.7	3.5	7.8	4.7	6.8	4.9	4.2	3.0	3.9	3.6	2.7	4.7	3.8	5.0
%O as OH	5.7	3.7	0.8	5.1	2.9	-				3.9	1.4	0.5	2.8	0.8	0.4			
O/OH total, %	61	45	13	74	52	-				80	31	12	72	20	10			
V.M.	40.5	82	14	34.7	71	15	32	59	23	33	70	15	30.6	41	15	28	37	19
Density (He)							1.30	1.19	1.39							1.30	1.27	1.39
Refr. index (5460A°)							1.84	1.67	1.95							1.90	1.82	2.01
Atoms Br. added/100C (N.Br-suc- cinimide)				13		13				14	17	2.0	8.5					

Note: V = vitrinite, E = exinite, F = fusinite, M = micrinite.

they are thermally unstable, and in carbonization at a more normal rate of heating they would undoubtedly decompose in situ to a considerable extent.

The temperature of maximum rate of volatile evolution is about the same for exinites and micrinites as for vitrinites^{12,17}. Ladam and Alpern carbonized a vitrinite concentrate and an exinite concentrate from the same coal seam at 600° and made a detailed analysis of the volatile products by vapor-phase chromatography. They found the products from the exinite concentrate to contain much more aliphatic material, more benzene homologues, more side-chain-substituted aromatics and less phenols. This result is in accord with the differences in structure believed to exist between the starting materials, and implies that the process of thermal decomposition does not, at least in their conditions, blur the effects of differences in structure.

It is well-known that the C-O bond in phenols is considerably weaker than the C-C, and that the C-H bond in the aliphatic parts of hydroaromatics is weaker than aromatic C-H. It is therefore reasonable to suppose that when molecules of the type attributed to vitrinites are heated, the primary changes will be homolytic dissociation of OH groups and loss of hydrogen from naphthenic rings, the latter resulting in thermal aromatization. It is likely that in an assembly of large complex molecules of the type described, where the changes of configuration required by aromatization may be difficult, that some of the hydroaromatic bridges will split rather than dehydrogenate; this may be the means whereby the aromatic material found in tar is broken off the main structure. These various changes will produce in the first instance OH radicals and H atoms, and leave free radical centres in the main structure, which would initiate further rearrangement and decomposition.

It is well known that little molecular hydrogen is evolved from coals until temperatures near 600° are reached. The hydrogen released by thermal dehydrogenation at lower temperatures must be consumed in saturating free radical centres in the volatile matter and the residue.

These ideas receive some confirmation from a series of experiments on the pyrolysis of model substances reported by van Krevelen and his co-workers²⁵. These authors synthesized a number of polymers containing various substituted and unsubstituted aromatic nuclei linked and cross-linked by methylene bridges. They found that, on pyrolysis, unsubstituted hydrocarbon polymers showed a maximum rate of decomposition at about 500°, and split extensively at the bridge units, leaving little solid (coke) residue. On the other hand polymers containing naphthenic rings, or still more if they contained phenolic hydroxyl substituents, showed a maximum rate of decomposition at considerably lower temperatures and left a much greater amount of coke residue. They concluded that when substituents are present there is, competing with the normal depolymerization reaction, a direct condensation proceeding as a result of dissociation of the substituents, and the latter tends to produce molecular enlargement. In support of this suggestion of competing reactions they adduce the fact that when substituents are present the coke yield increases greatly with decreasing rate of heating.

There is one other factor that should be mentioned. The late D. H. Bangham pointed out²⁶ that volatile matter evolved inside a particle of coal may well have to diffuse in a mobile adsorbed film in fine pores to the outside; while so adsorbed it is exposed to surface forces that could promote secondary reactions and also could act as a lubricant in promoting fluidity. Since porosity varies with rank, passing through a minimum at a carbon content about 89%, the magnitude of these effects will also vary with rank.

There is no experimental evidence bearing on the chemistry of the pyrolysis of the inert macerals. From the nature of this structure one would deduce that some

stripping of peripheral groups would occur, permitting condensation with neighboring molecules, but little alteration of the basic skeletal structure. The behavior of inert macerals as seen with the hot stage microscope is beautifully demonstrated in the color film prepared by W. Spackman and his collaborators. Exinitic material can be seen to liquefy and flow round grains of inertinite, the morphology of the latter remaining almost unchanged.

A Chemical Description of Carbonization

A synthesis of the information given above permits a fairly detailed description of the main chemical phenomena of carbonization. The first major change is a softening of the "volatile solids", in Dryden's terminology, which, it is suggested, represent the lower molecular weight, hydrogen-rich, fraction of the coal. This softening is accompanied by the initiation of the decomposition of this fraction, and perhaps also of the involatile residue, the primary step being dissociation of hydrogen from hydroaromatics, shortly followed by dissociation of OH. These chemical changes cause two principal secondary reactions, one leaving a more aromatic hydrogen-poor material and the other a breaking off of volatile partly aromatic fragments as a result of the destabilization of the main structure owing to radical formation in it. A limited amount of cross-linking may also occur, giving a more stable and less volatile residue. These various changes, initiated by dissociation of H and OH, are more or less complete by about 500-550°. By this stage, much of the oxygen has been stripped off and the aromatic nuclei have not grown much in size but the molecules are more highly cross-linked. Some of the free radical centres produced by decomposition remain as such, "trapped" in the carbon matrix.

At 600-650° enough energy is available to break a few aromatic carbon-carbon bonds, so that the carbon skeleton can rearrange and condense to larger polycyclic nuclei of lower H/C ratio, and hydrogen gas is released. These changes also permit the pairing of the odd electrons in the free radical centres. The dramatic change in electrical conductivity no doubt results partly from the growth of the aromatic lamellae, partly from the elimination of insulating material between the lamellae, and partly from a greater degree of order in their stacking.

These changes no doubt continue at a diminished rate at higher temperatures still, and some of the oxygen, nitrogen and sulfur is stripped out.

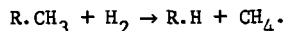
This description probably has some application to sporinites also. But it has been suggested that there may be an additional factor here¹³. The greater interlayer spacing in exinites and the less polar nature of the molecules will cause the intermolecular forces of adhesion to be weaker than they are in vitrinites. This may be an important cause of the greater fluidity of exinites and the facility with which volatile matter escapes. Moreover, it will change the balance between van Krevelen's competing reactions, that is, the direct breakdown and the condensation to larger units resulting from dissociation of H and OH. In any case the ratio of hydroaromatic hydrogen to hydroxyl is much greater in exinites than vitrinites.

Discussion and Conclusions

The relevance of the above information and speculation to the production of chemical by-products from coal will be discussed with reference to hydrogenation, carbonization, and other methods.

(a) Hydrogenation

It is possible by use of a carbon catalyst, an elevated temperature, and a high partial pressure of hydrogen, to cause hydrogenolysis of alkyl groups in alkyl aromatics without saturating the ring; for example:



Ideally, this is in effect what one would wish to do in the hydrogenation of coal; the hydroaromatic parts of the structure would be eliminated as methane and ethane and the individual aromatic nuclei would be released as a mixture of relatively simple phenols, hydrocarbons and perhaps quinones or quinols. However, if the 1,2-cyclohexadiene type of linking unit, as in 9,10-dihydrophenanthrene, were common, stable single linkages between aromatic nuclei would remain in the product. Thus for example dihydrophenanthrene itself would give diphenyl and ethane, whereas the isomeric dihydroanthracene would give benzene and methane.

There are of course practical difficulties in contacting solid coal with a solid catalyst. For this reason, and because of the complexity of coal structure, such selectivity of hydrogenolysis is improbable. It is more likely that partial or complete saturation of the aromatic nuclei will precede any extensive hydrogenolysis of the linking units. Once saturation occurs, we are left with an extended naphthenic structure in which there is nothing to distinguish between the linking and aromatic parts of the original structure (except perhaps some oxygen substituents and heterocyclic atoms).

Perhaps, then, from a chemical point of view the best hope of breaking down coal structure to useful products by hydrogenation is to proceed in two steps, first a catalytic addition of hydrogen to the aromatic parts, and then a cracking, perhaps with a conventional cracking catalyst in a high-boiling oil.

The above remarks should apply equally to exinitic material. In carbonization one needs, in order to make a good coke, an optimum fluidity and not a maximum. In view of the difficulties of reactions involving two solid phases, in hydrogenation the maximum fluidity is clearly desirable, and so the greater the exinite content of the raw material the better. Indeed it would be desirable, if economically feasible, to use a blend of a coal with a black durain or other exinite concentrate.

On the other hand the inert components are too graphitic to be at all readily hydrogenated and broken down, and inasmuch as they will tend to decrease fluidity are undesirable contaminants of the raw material for hydrogenation.

(b) Carbonization

Carbonization of coal is carried out in the U.S.A. almost entirely for the purpose of making coke, and it is doubtful how far the process can be modified merely to improve the yield or quality of by-products. However, since the purpose of this paper is to discuss the basic chemistry involved, this factor is ignored in what follows.

It seems likely that both the total yield of chemicals from coal carbonization and the content of useful materials will increase with the exinite content of the charge, even though in commercial operation the volatile matter is exposed to much secondary change. Since the yield of volatile matter from exinites is so much (50-100%) greater than that from vitrinites, the relatively small amount (10-25%) commonly found in whole coals charged to coke ovens can make a very significant contribution to the volatile matter collected. Moreover the differences in behavior between different coals of apparently similar rank may be due in part to differences in their content of sporinite and resinite. The inert macerals will decrease the yield, not merely because they are relatively inert diluents but also because they are likely to be efficient free radical traps in the early stages of the release of volatile matter.

Coking blends commonly contain the basic coal to provide the bulk of the coke matrix, a component designed to increase fluidity to the desired extent, and an inert diluent to increase the coke hardness. Clearly there are likely to be a range of three-component mixtures that will give the desired result. It is at least a theoretical possibility that one could select a mixture within the range such that inertinite is used as little as possible as an inert diluent and exinite-

containing material is used both to contribute fluidity and to increase the yield of by-products.

If still further departures from present practice can be considered, one might carbonize, perhaps in a fluidized bed, in the presence of additives. Additives could be gaseous and include steam and a little air, or be a solid and consist of a catalyst designed to assist the breakdown of volatile matter to simpler material immediately on release from the coal particles. In any case if one wishes to interfere with the carbonization mechanism in this or in any other way, one must obviously do it in the dissociation stage (380-480°) or earlier.

(c) Other Methods

At one time it was thought that coal might be like a polymer in containing a variety of monomer units linked together by a relatively weak bond, as in cellulose. This view can no longer be maintained; in so far as it is just to consider coal a type of polymer, the linking units are not weak but very strong. The hopes of finding a simple economically feasible means of breaking the structure down into useful chemicals as main rather than by-products are therefore small. The depolymerization of coal with the boron trifluoride/phenol complex, described by Heredy and Neuworth,¹¹ is a very interesting contribution to this problem and will no doubt be developed further.

The classical organic chemist's answer to the problem of breaking down a mixed aliphatic-aromatic structure is selective oxidation of the aliphatic parts. It has so far proved impossible to oxidize coal selectively in this sense, but in any case a range of aromatic acids will be the principal products; these may have practical applications, but necessarily only in a strictly limited field. The fluorination procedure described by Farendon and Pritchard²⁷ is another reaction that might give chemical products useful in a limited field.

Provided the bulk of the products could be sold at chemical rather than fuel prices, it might be possible to use exinite concentrates as raw materials for chemical processing, and they possess certain advantages. This is a possibility that should be explored further. The cannel and boghead coals are described as being largely exinite, but in view of their different origin it seems doubtful whether they are very similar to the exinite material associated with bituminous coals. However, they might be useful starting materials.

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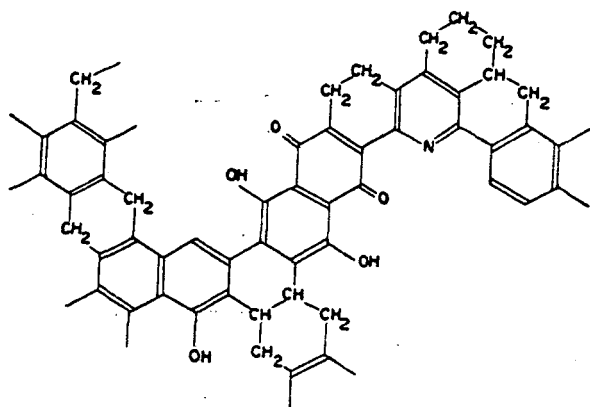


FIGURE 1. *Hypothetical segment of a typical molecule in a bituminous coal.*

THE COMPOSITION OF HIGH TEMPERATURE COKE OVEN TARS

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Introduction

Until 1882 crude gas works tar was the only type produced in Great Britain since, up to that time, coking plants were not equipped for the recovery of by-products. The by-product coke oven was first developed in France and introduced at about the same time in Germany, Belgium and England. Its use, coupled with the oil washing process for benzole recovery which was introduced by Carvès in 1884, was extensively adopted in Continental Europe but it took twenty years for the advantages of by-product coke ovens to be appreciated in England. Since then, however, coke oven tar production has increased year by year reaching a peak in 1957 of 1,250,000 tons. For those interested in statistics the following table shows the production of coke oven tar in the United Kingdom in the years 1950 - 1960.

Table 1
Production of Coke Oven Tar in the U.K. 1950 - 1960

Year	Tonnage Produced	% of all Tar Produced
1950	931,127	35.55
1951	977,379	35.64
1952	1,032,361	36.22
1953	1,056,767	37.10
1954	1,095,085	37.37
1955	1,101,294	36.76
1956	1,191,129	38.33
1957	1,252,079	40.27
1958	1,164,554	40.03
1959	1,096,399	40.40
1960	1,187,205	42.42

About 150,000 tons of crude coke oven tar is burned, the remainder is distilled for the manufacture of pitch, creosote, naphthalene, anthracene, some benzene, toluene, xylenes and naphthas and phenol and cresylic acid. It will be noted that coke oven tar accounts for about two-fifths of the total tar production in the U.K. The remainder in 1960 was made up of continuous vertical retort tar (42.85%), intermittent vertical retort tar (4.05), horizontal retort tar (5.42%), low-temperature tar (2.08%) and other types (1.17%).

Coke oven tar thus represents an important raw material whose chemical composition has been the subject of considerable study during the past sixty years. To date some 400 individual components have been isolated or identified and it is probably safe to say that at least that number are still unidentified. The vast majority of the components are present in very small amounts and can never be of any commercial interest. It is not the intention in this paper to recite a catalogue of the known components of high-temperature tars; many exhaustive compilations exist, one of the most comprehensive and complete being that compiled by K.C. Linepensel of Koppers Co. Inc.

Assays of Coke Oven Tars

Until recently, published analyses of coke oven tars took the form of distilling the crude tar under rather empirical conditions into arbitrary fractions which were intended to simulate the fractions obtained on commercial practice. Frequently these fractions were given non-specific names like "light naphtha", "light creosote", "carbolic oil" etc. and the content of major components such as naphthalene or phenol recorded were not those actually occurring in the crude tar but the amounts of the component (frequently impure) which crystallized from, or could be extracted from, one of these fractions. Since the distillation conditions and the degree of fractionation, the boiling ranges of the distillate oils and the method of analysis of these oils for individual components differed for each worker, it is impossible to compare the results of most of the published assays of coke oven tars and they contribute comparatively little to our knowledge of its actual chemical composition.

A few assays of coke oven tars which determine the actual amounts of commercially important components present have been published, for example the examination of American coke oven tar by Weiss and Downs¹ and of Australian coke oven tars by workers at the Coal Research Section of the Commonwealth Scientific and Industrial Research Organisation.² Assays of this type on a representative selection of U.K. coke oven tars have been carried out by The Coal Tar Research Association during the past eight years and it is these which are described and discussed in greater detail below.

The C.T.R.A. Assay Method

Preliminary work showed that the first stage of the method could be either accomplished by solvent extraction or by distillation without altering the yields of products except the pitch yield and the amount of tar acids and tar bases. It was shown that about one third of the tar acids are retained as complexes with tar bases in the residue on solvent extraction and are not

subsequently determined in the extract. Distillation was therefore chosen as the preliminary fractionation procedure and the conditions selected were those which, by trial and error, gave the same yield of medium soft pitch (70°C K & S) as was obtained from the same tar on continuous distillation in a Wilton pipe still.

5.5 kilos of the crude tar are placed in a cast iron pot and heated gently to 200°C to remove water and light oils. The latter are then fractionated on a 30 plate low hold-up column to give benzole (up to 100°C), toluole (100-125°C) and xylole (125-150°C). The residue from this distillation is added back to the dehydrated tar in the pot still and distillation continued at a rate of 14 g./minute until the vapour temperature reaches 358°C.

The oils from this primary separation step are then washed with alkali and acid to recover tar acids and tar bases respectively and the neutral oils fractionated on a 50 plate column at progressively reduced pressure to yield seven fractions and a residue as follows:-

Fraction 1	Naphtha fraction	Boiling Range	150°C/760mm. - 137°C/100 mm.
Fraction 2	Crude Naphthalene fraction	" "	137°C/100mm. - 145°C/100 mm.
Fraction 3	Methyl Naphthalene Oil	" "	145°C/100mm. - 155°C/50 mm.
Fraction 4	Diphenyl Oil fraction	" "	155°C/50mm. - 168°C/50 mm.
Fraction 5	Acenaphthene Oil fraction	" "	168°C/50mm. - 184°C/50 mm.
Fraction 6	Fluorene Oil fraction	" "	184°C/50mm. - 150°C/20 mm.
Fraction 7	Anthracene Oil fraction	" "	150°C/20mm. - 200°C/5 mm.
Fraction 8	Heavy Oil Residue		

Each of these fractions is then analysed by suitable chemical, spectroscopic and/or chromatographic methods for the quantitative determination of its major components.

The extracted tar acids are also subjected to high efficiency fractionation and the individual fractions analysed by gas-chromatography for phenol, cresol isomers and xylenols.

The practical details of this method have been published³ and are not given here.

The Results of Assays of British Coke Oven Tars

For the purpose of this paper it will be sufficient to set down the highest, lowest and mean values obtained for the content of major constituents in British coke oven tars. This is done in Table 2. For comparison the corresponding figures for some Canadian coke oven tars (average of 6) and one Australian coke oven tar carried out by the C.T.R.A. method are included.

Table 2

Amount of Components in British, Canadian and Australian Coke Oven Tars
(Results are given as wt. % on dry tar)

Source	British			Canadian			Australian
	Max.	Min.	Mean	Max.	Min.	Mean	
Benzene	0.42	0.124	0.252	0.297	trace	0.119	trace
Toluene	0.353	0.090	0.224	0.467	0.008	0.148	0.14
o-Xylene	0.071	0.020	0.037	0.133	0.005	0.038	0.15
m-Xylene	0.175	0.056	0.106	0.215	0.009	0.069	
p-Xylene	0.072	0.020	0.040	0.083	0.003	0.026	
Ethyl Benzene	0.05	0.005	0.02	0.04	0.01	0.02	
Styrene	0.067	0.020	0.038	0.046	0.008	0.020	1.03
Phenol	1.15	0.14	0.57	0.98	trace	0.61	
o-Cresol	0.84	0.10	0.32	0.51	trace	0.25	
m-Cresol	1.00	0.16	0.45	0.84	trace	0.45	
p-Cresol	0.70	0.07	0.27	0.52	trace	0.27	0.25
Xylenols	1.30	0.13	0.48	0.85	0.01	0.36	0.34
High-Boiling							
Tar Acids	2.09	0.31	0.91	1.51	0.14	0.83	0.45
Naphtha	2.66	0.52	1.18	2.21	0.15	0.97	1.03
Naphthalene	11.31	7.29	8.94	15.30	3.08	8.80	9.44
α-Methyl Naphthalene	0.86	0.60	0.72	1.08	0.37	0.65	0.58
β-Methyl Naphthalene	1.63	1.15	1.32	1.76	0.65	1.23	1.16
Acenaphthene	1.28	0.42	0.96	1.27	0.71	1.06	-
Fluorene	1.80	0.46	0.88	1.29	0.47	0.84	1.90
Diphenylene Oxide	2.00	1.40	1.50	-	-	-	1.00
Anthracene	1.38	0.52	1.00	1.01	0.47	0.75	0.68
Phenanthrene	8.8	2.3	6.3	3.00	2.14	2.66	2.32
Carbazole	1.73	0.58	1.33	1.23	0.32	0.60	0.35
Tar Bases	2.60	1.25	1.77	2.90	1.68	2.05	1.34
Pitch (70°C K & S)	63.9	49.5	59.8	70.85	52.4	63.5	62.4

The immediately striking feature of these figures is the variation they show in the content of particular components. Thus the content of phenol and cresols found in British coke oven tars can vary by a factor of ten; naphthalene content can be as high as 11% or as low as 7% and the amount of pitch produced on distillation may be less than 50% or greater than 60%.

The reasons for these variations in the amounts of individual components in coke oven tars are not at present well defined. Qualitatively it may be said that the nature of the coal, the design of coke oven, the carbonisation conditions used and the nature of the recovery system at the carbonising

plant all play a part. The generally higher level of phenanthrene and carbazole in British tars compared with the Canadian tars or the Australian tars is almost certainly to be attributed to differences in the coal structure. Certain British and Canadian tars, which show a low content of components boiling up to 230°C (benzene, toluene, xylenes, naphthas, naphthalene and phenol), are products of plants which operate their by-product recovery system in such a way that more of the volatile carbonisation products are scrubbed from the gas and less precipitated as tar. Generally speaking high naphthalene content, high pitch yield and low tar acid content go hand-in-hand, except for tars produced from low volatile coals e.g. Welsh steam coals. These are characterized by a high naphthalene and phenanthrene content but a low pitch yield.

It may be noted in passing that the tars produced in continuous gas-works vertical retorts are much more uniform in composition.

The large variations in the content of valuable components which can occur in coke oven tars is of more than theoretical significance. To the operator of coke ovens tar is tar, an unwanted by-product which he seeks to get rid of in any way he can. But to the tar distiller it is the raw material which must be transformed into products which can be sold at a profit. Changes in operation or in the blend of coal carbonised may occur at coke ovens which affect the nature of the tar produced. The first indication which the distiller has of these changes is when his fractionating column is thrown out of balance or when his naphthalene or tar acid production mysteriously drops. His first reaction is to suspect that his distillation and recovery plant have fallen in efficiency and he frequently spends some frustrating days - or even weeks or months - trying to locate non-existent faults.

These considerations suggested that there was a real need for some simple and rapid method of analysis and characterization of tars by which the tar distiller could check whether any major variation in his raw material had occurred.

Characterization of Tars

With this object in view a study of all tars in the storage tanks of British tar distillers was carried out some time ago. The idea behind this study was to analyse these tars by simple and, as far as possible, rapid methods and to see, by a statistical analysis of the results, which properties showed some correlation. It was hoped that, by selecting a few key properties with which other properties are correlated, some suitable characterization index could be derived.

In all 61 tars, of which 21 were from coke oven installations, were received and the analysis method, which has been described in detail,⁴ consisted in dehydrating the crude tar, determining the specific gravity and solvent analysis of the dry tar which was then subjected to a standard distillation to yield three distillate oil fractions, - 0-250°C, 250-300°C and 300°C - pitch and a 70 ± 2°C (K & S) residue. The distillate oils were analysed for tar acid content,

paraffin content and naphthalene content and the pitch was analysed for C/H ratio and subjected to a Mallison solvent analysis for its content of H- and M-resins.

Statistical analysis of all the results showed that the most useful index was the specific gravity of the dry tar. This gave a high degree of correlation with the pitch yield (in fact this relationship was used to determine the end point of the distillation to leave a pitch of the desired softening point) (Fig.1); it also showed a good correlation with the viscosity of the dry tar (Fig.2) and with the C/H ratio of the pitch. For the full range of tars (coke oven tars, continuous vertical retort tars, intermittent vertical retort tars, horizontal retort tars and blended tars) the correlation coefficients between specific gravity of the tar and paraffin content, specific gravity of the tar and phenol content and between phenol content and naphthalene content were statistically significant but, if the analysis was confined to coke oven tars, these correlations and that between the paraffins and tar acids or those between any of these properties and the naphthalene content were not significant as will be appreciated from the almost random distribution of points in Figures 3 and 4.

Although a characterization index was suggested based on three numbers indicating the level of dry tar gravity, phenol content of the 0-250°C distillate and the benzene insoluble content of the dry tar, this index is not of particular value in detecting changes in coke oven tar supplies to a distillery. It has proved of value in detecting changes in gas works carbonising practice and in anticipating changes in plant operation when the ratio of different types of tar in a blended feedstock is altered but it must be admitted that the problem of a simple characterization procedure for coke oven tars is still unsolved. The variations in properties of the coke oven samples examined are indicated in Table 2. This gives the maximum, minimum and mean values for the properties determined and also lists those properties for the coke oven tars with the highest and lowest phenol, paraffin and naphthalene contents (tars A1, A2, B1, B2, C1 and C2).

Table 2

Property	All Coke Oven Tars			Tar A1	Tar A2	Tar B1	Tar B2	Tar C1	Tar C2
	Max.	Min.	Mean						
Sp.Gr. of Dry Tar at 20°C	1.218	1.141	1.188	1.141	1.209	1.184	1.203	1.185	1.217
Viscosity of Dry Tar (Redwood No.1 secs at 60°C)	1.971	172	723	253	1247	382	546	438	1971
Wt.% Oils to 250°C	15.6	6.7	12.1	15.2	8.0	14.7	10.0	13.5	7.8
Wt.% Oils 250-300°C	12.2	9.3	11.30	12.2	9.4	9.7	9.7	12.2	9.6
Wt.% Pitch	69.2	52.2	61.0	52.2	66.8	59.3	62.9	59.1	68.6
% Phenols in Oil to 250°C	19.7	nil	7.8	19.7	nil	6.2	nil	9.2	9.5
% Paraffins " " "	2.3	nil	0.9	2.1	0.2	2.3	nil	1.8	0.8
% Naphthalene in Dry Tar	10.5	6.4	9.1	6.8	8.4	9.1	9.9	10.5	6.4
% Benzene Insoluble in Dry Tar	12.1	4.1	8.5	4.3	9.4	7.4	11.3	11.8	10.0

The Chemical Composition of Coke Oven Tar Distillate Oils

It is only recently, with the development of vapour chromatography, that it has been possible to obtain any information on the quantitative composition of tar distillate oils. The data so far obtained are, however, scanty and incomplete, mainly due to the limited number of reference compounds available for calibration of chromatographic columns.

Benzoles and Naphthas

Coke oven tar oils boiling up to 150°C which have been washed free from tar bases are remarkably uniform in composition. Their major components are benzene, 33-40%; toluene, 24-33%; m-xylene, 10-15%; o-xylene, p-xylene and styrene, about 5% each, ethyl benzene about 2% and thiophene and methyl thiophenes 1-2%. Non-aromatics which may occur in amounts up to 5%, are mainly methyl cyclohexane.

In the naphtha range (150-200°C) the main neutral components are indene, hydrindene, coumarone and pseudocumene with smaller amounts of ethyl toluene, mesitylene and hemimellitene and an amount of paraffins varying from a trace to 5%. In some samples n-propyl benzene is detectable and there is generally up to 15% naphthalene and some methyl naphthalenes depending on the efficiency of the fractionation procedure. The ratio of the components boiling up to 200°C varies considerably as is shown in Table 3 which lists the maximum, minimum and mean values.

Table 3

Composition of Coke Oven Coal Tar Naphthas (150-200°C boiling range)

Component	Wt. %		
	Max.	Min.	Mean
n-Propyl Benzene	3.9	nil	0.6
meta & para ethyl Toluenes	8.5	0.4	2.8
Mesitylene	6.5	0.8	3.2
Pseudocumene	14.8	3.7	8.7
Hemimellitene	6.9	trace	2.9
Hydrindene	46.5	12.7	28.9
Indene	53.0	10.0	38.2
Coumarone	15.9	5.2	11.0
Paraffins	10.0	nil	3.7

Naphthalene Oils

By far the major component of the tar-acid free coke oven oils boiling in the range 200-250°C is naphthalene which in well fractionated samples may be 65% of the tar-acid free oil. The remaining 35-50% is made up of thionaphthene 2-3%, α -methyl naphthalene 6-10%, β -methyl naphthalene 15-20%, quinoline 2-5%, paraffins, mainly dodecane 0-2% and amounts of dimethyl naphthalenes, dimethyl hydrindenenes and acenaphthene.

Oils Boiling in the 250-300°C Range

The analysis of coke oven wash oils and light creosotes which have so far been carried out indicate that in this range the main constituents are, as would be expected, acenaphthene, diphenylene oxide and fluorene and these three components account for at least 50% of the fraction. The remainder is very complex with numerous minor unidentified compounds. Diphenyl and dimethyl naphthalenes make up 10-20% of this range and some of the trimethyl naphthalenes have been identified in it.


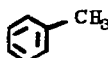
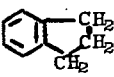



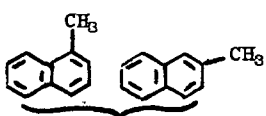
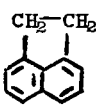
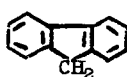
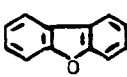
Anthracene Oils and Heavy Oils

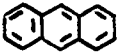

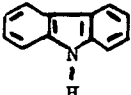
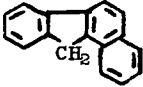
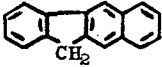
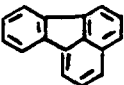
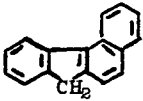

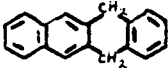
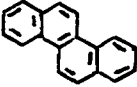
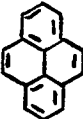
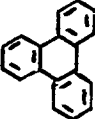
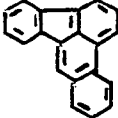
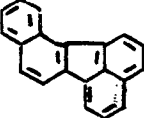
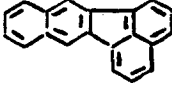
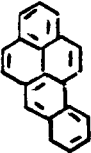
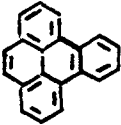
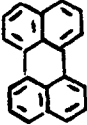
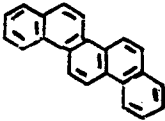
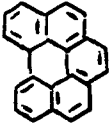
Phenanthrene, anthracene and carbazole make up on the average 75% of the coke oven tar fractions distilling from 300°C to 350°C. Phenanthrene is by far the major component, there being 6-8 times as much phenanthrene as anthracene; carbazole content is generally somewhat higher than that of anthracene. The remaining 25% consists of a large number of minor components which include tri- and tetra-methyl naphthalenes, diphenylene sulphide, phenyl-naphthalenes, acridine, methyl fluorenes and dimethyl diphenylene oxides.

Coke Oven Pitch

As the boiling range is ascended the complexity of coke oven tar fractions increases and their analysis becomes more difficult. Not only are the limits of volatility for fractionation reached but the value of analysis by vapour chromatography becomes increasingly limited by the lack of reference compounds. 45-55% of coke oven pitch can be separated from the remainder either by exhaustive extraction with petroleum ether or by vacuum distillation. These fractions have average molecular weights in the range 200-300 and appear to contain about one OH group per ten molecules and one CH_2 or CH_3 group for every three molecules. NH groups occur once in every ten molecules and =N- groups once per 8 molecules. Vapour chromatography on a high-temperature column shows the main hydrocarbon components to be fluorene, anthracene, phenanthrene, pyrene, chrysene, fluoranthene, benzfluorenes, benzfluoranthenes, benzpyrenes, perylene, benzperylene and picene.⁵ These compounds, together with brazan, dihydronaphthacene, triphenylene are the compounds which can be isolated most readily from coke oven pitch distillates or solvent extracts.

At this stage it is worth while setting down the major hydrocarbon components of coke oven tar in order of their complexity. This gives the following picture:-

Boiling Range	Average % of Tar	Major Components		
0 - 150°C	0.8			Single 6-membered rings
		Benzene	Toluene	
150 - 200°C	2			
		Hydrindene	Indene	Coumarone
200-250°C	12			Fused 6,6-ring systems
		Naphthalene	Methyl Naphthalenes	
250-300°C	8			
		Acenaphthene	Fluorene	Diphenylene Oxide

Boiling Range	Average % of Tar	Major Components			
300-350°C	15				Fused 6,5,6- and 6,6,6- ring systems
		Anthracene	Phenanthrene	Carbazole	
Pitch Crystalloids	32				Fused 6,5,6,6- ring systems
		1,2-Benzfluorene	2,3-Benzfluorene		
					
		Fluoranthene	3,4-Benzfluorene	Brazan	
					Fused 6,6,6,6- ring systems
		Dihydronaphthacene	Chrysene	Pyrene	
					
				Triphenylene	
					Fused 6,6,5,6,6- ring systems
		2,3-Benzfluoranthene	7,8-Benzfluoranthene	8,9-Benzfluoranthene	
					
		1,2-Benzpyrene	4,5-Benzpyrene	Perylene	
					Fused 6,6,6,6,6- ring systems
				Picene	
					Fused 6,6,6,6,6,6- ring systems
		1,12-Benzperylene			

It would be expected that the remaining thirty odd per cent of pitch - the resinoid, C_2 and C_1 fractions - would extend this logical sequence, the number of fused rings in the main components increasing from six to a considerably high value. There is still, however, some controversy about the molecular weight of these fractions. Values obtained at C.T.R.A. by osmotic pressure measurements and by ebullioscopic determinations in benzene and pyridine vary from 400

1200 for fractions of the resinoids with an average value of about 550 and from 1000 - 1500 for the C_2 fraction (i.e. the benzene insoluble-pyridine soluble fraction). Other workers have recorded much lower values. These lower values we believe to be due to the presence of low molecular weight material in the fractions analysed either due to the imprecise nature of the fractionation method adopted, or more probably, to the incomplete removal of solvent from the recovered fractions.

If the results which Wood⁵ gives for the fractions of a coke oven pitch, separated by a precise and reproducible solvent fractionation, are accepted and subjected to statistical structural analysis in the same manner in which van Krevelen and his co-workers^{3, 7} have considered coal macerals, the conclusions are that the more complex fractions of coke oven pitch form a logical extension of the series formed by the distillate oil fractions.

In carrying out this analysis certain assumptions must be made. For example it is assumed that both -NH- (determined by potentiometric titration with perchloric acid), -N- (determined from total nitrogen content, less the -NH- groups) and -O- groups (determined by subtracting -OH groups from the total number of oxygen atoms in the average molecule) are present in ring systems. Hydrogen which cannot be accounted for as -OH , -NH- or aromatic -CH (determined from the infra-red absorption at 3050 cm^{-1}) are assumed to be equally divided between CH_2 and CH_3 groups. By van Krevelen and Chermis's⁶ "lift out and replace principle" an equivalent hydrocarbon structure may be calculated and the aromaticity (Ar) i.e. number of "equivalent" ring carbons divided by total "equivalent" carbons calculated. The number of rings in the average molecule can be derived from the formula:-

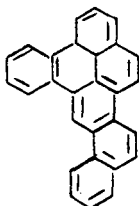
$$\text{Ar} = \left(1 - \frac{\text{H}}{\text{C}}\right) + \left[1 - \frac{2(\text{R}-1)}{\text{C}}\right]$$

and by subtracting the number of "equivalent" ring $\text{-CH}_2\text{-}$ groups and the number of $\text{-CH}_2\text{-}$ and -CH_3 groups from the total number of "equivalent" C atoms, a figure is obtained for the number of C atoms at the junction of fused rings.

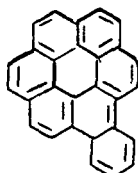
The largest fraction - that soluble in heptane-dioxan - has a molecular weight of 220, an average formula of $\text{C}_{15.7}\text{H}_{11.7}\text{O}_{0.21}\text{N}_{0.22}\text{S}_{0.07}$ and an "equivalent" hydrocarbon structure of $\text{C}_{17.1}\text{H}_{12.3}$. Its aromaticity is 0.98, the average number of rings per molecule is 3.6 and the number of ring joining carbon atoms per molecule is 5.3 which suggests an average degree of condensation similar to that found in pyrene. These results are consistent with what other data are available for the structure of pitch crystalloids.

The next major fraction which makes up 10% of the pitch is that soluble

in heptane and this has a molecular weight of 400, a molecular formula of $C_{29.3}H_{19.5}O_{0.93}N_{0.49}S_{0.14}$. It contains on the average 7 rings per molecule, an aromaticity of 0.923 with, on the average 2.13 CH_2 or CH_3 and 0.19 OH groups per molecule. The number of ring-joining atoms is 11.9 which for 28.6 equivalent ring carbons (C_R) is close to $\frac{C_R}{2} - 3$ and consistent with a structure such as I rather than II.

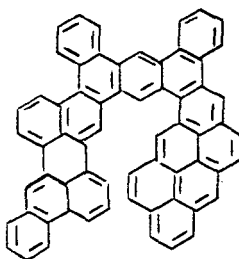


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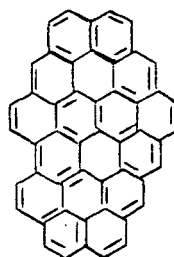


II

The next major fraction is that insoluble in methanol but soluble in benzene whose number average molecular weight is 910 and whose molecular formula is $C_{88.5}H_{41.0}O_{1.49}N_{1.04}S_{0.31}$. It has an aromaticity of 0.92 and the average number of rings in the molecule is 17.4. Ring joining carbons total 31 and the equivalent ring carbons 64.8. This again is more consistent with a "ring-chain", fairly open structure than a closely packed, highly condensed structure. Thus the seventeen ring aromatic system, III has 64 ring carbons and 32 ring joining carbons against 50 carbon atoms and 32 ring joining carbons for the highly condensed system IV.



III



IV

It is, however, only right to point out that the two smaller fractions of the pitch amounting to 1.3 and 3.4% of the pitch respectively do not fit into the series; it is, however, believed that the analytical results on these are unreliable because of adsorbed solvents.

Tar Acids

65 to 70% of the tar acids extracted from the distillate oils are made up of phenol, cresols and xylenols, the distribution being as indicated in Table 4.

Table 4Composition of Phenols Extracted from Coke Oven Oils

Tar Acid	wt. % of Total		
	Max.	Min.	Mean
Phenol	30	14.3	19.0
o-Cresol	11.3	8.7	9.8
m-Cresol	16.3	13.5	14.8
p-Cresol	9.5	7.1	8.2
Xylenols and ethyl phenols	17.6	6.4	14.1
Higher Boiling Tar Acids	36.9	28.7	34.1

The higher boiling tar acids are a complex mixture of which the major constituents are 3-methyl-5-ethyl phenol, 2-methyl-4-ethyl phenol, 4-indanol, 5-indanol, 6-methyl-4-indanol, 7-methyl-5-indanol, α -naphthol and β -naphthol.

Tar Bases

No complete analysis of the bases extracted from the distillate oils of British coke oven tars is as yet available. According to the C.S.I.R.O. workers² the bases from an Australian coke oven tar contain 33.17% quinoline, 8.28% isoquinoline, 8.92% quinaldine, 0.91% 8-methyl quinoline and 3.21% 6-methyl quinoline.

The General Structure of Coke Oven Tars

The data given in this paper indicate that high-temperature coke oven tars are complex mixtures of aromatic and heterocyclic ring compounds. At the lower end of the boiling range single six-membered ring systems occur, with their corresponding hydroxy and alkyl substituents and the alkyl groups, while predominantly methyl, include ethyl and n-propyl side chains. Single ring compounds make up, however, less than 5% of tar. They are followed, as the boiling range is ascended, by fused six and five membered ring systems with their corresponding methyl and hydroxyl substituents; such systems, however, again make up less than 5% of the total. The next members of the ascending series - molecules containing two fused six membered rings, two six membered rings and one five membered ring, or three fused six membered rings - are major constituents making up some 30-35% of the tar. In this range naphthalene and phenanthrene are the major components with the other unsubstituted aromatic

compounds, acenaphthene, fluorene and anthracene, also prominent. Methyl and dimethyl derivatives of these aromatic hydrocarbons and the corresponding heterocyclic compounds occur as minor constituents. Oxygen compounds with the oxygen in a five membered ring are the most common heterocyclic compounds followed by tertiary bases with the nitrogen in a six membered ring system or as $-NH-$ in a five membered ring.

The same pattern is preserved in the pitch oils which make up about 30% of the tar. These consist predominantly of unsubstituted aromatic hydrocarbons containing from four to seven or eight fused rings and, in general, the ring systems are not fully condensed. Methyl and hydroxy substituents are rare but do occur and about ten per cent of the molecules contain a heterocyclic oxygen, nitrogen or sulphur atom in the ring system in this order of abundance. Compounds containing more than one heterocyclic atom are rare and, although polyphenyl compounds are present, they are very minor components. Compounds with partly substituted ring systems are also present in small amount but in most of the compounds containing ring $-CH_2-$ groups, the $-CH_2-$ is part of a five membered ring.

The most complex 30% of pitch represented by the pitch resins and the so called C_2 and C_1 fractions appears, from our present knowledge, to be a continuation of the series formed by the less complex and more volatile fractions and consists essentially of ring compounds containing from 8 to more than 20 rings in the molecule. The evidence, however, points to the fact that these more complex constituents have ring systems which are not highly condensed but rather consist of highly branched ring chain structures in which the majority of the rings are fused to no more than three other rings.

As further evidence of the relatively low degree of condensation in the ring structure of the molecules in pitch, may be cited the fact that the infra-red spectra of pitch fractions shows much stronger bands at 750 cm^{-1} due to ortho substitution in the aromatic ring than at the other wave lengths characteristic of other types of substitution, indicating that there are a fair number of unsubstituted end-rings i.e. rings fused to only one other ring.⁵

The Composition of Tars and the Structure of Coal

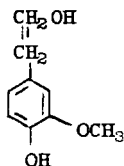
It has been said that the products of carbonisation of coal have about as much resemblance to the original coal structure as the fragments of ash from a burning library bear to the original books. On the other hand tar accounts for 15% of the coal structure in low-temperature carbonisation and, despite the complexity of the reactions occurring in the carbonisation process, some inferences as to the nature of the coal "molecule" should follow from a study of the composition of the tar.

This approach has been made by Karr and his co-workers^{8 9} on the basis of the divergence between the determined distribution of isomers in low-temperature tars and the predicted thermodynamic and kinetic distributions at the temperature of carbonisation. Karr's argument is that the tar produced

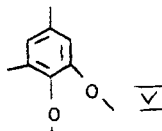
in low-temperature carbonisation of coal may be regarded either from the standpoint of thermodynamic equilibria or chemical kinetics. If thermodynamic equilibrium has been achieved the proportion of various isomers will be that predicted by theory. If the residence time is too short to enable equilibrium to be achieved the most abundant isomers should be those predicted from the relative rates of formation. Isomeric distributions outside the range predicted by the combined thermodynamic and kinetic systems might indicate dependence on the coal structure.

An examination of the distribution of alkyl benzenes, alkyl phenols, phenyl pyridines, methyl quinolines and substituted anilines found in low-temperature tars showed very considerable differences from the distributions predicted on either thermodynamic or chemical kinetic considerations. Particularly striking was the relatively high proportion of para isomers in structures for which thermodynamic equilibria predicted a preponderance of the meta isomer and kinetic consideration a preponderance of the ortho compound. There seemed, therefore, some justification for the suggestion that these isomers derived from some common monomeric unit of the coal structure. One such unit which would account for the isomeric distributions found and whose occurrence when coal is carbonised would be biogenetically plausible is 4-n-propyl-2-methoxy phenol derived from lignin which has been subjected to the coalification process.

Prior to Karr's publications a similar idea had been put forward, although not published, by W. Waddington of The Coal Tar Research Association. His suggested structure of that part of the coal molecule from which tar is derived was that of a polymer consisting of a long paraffinic or conjugated chain from which at intervals were attached 4-alkyl-2-methoxy phenol units, substituted in the 6-position by other paraffinic or conjugated side chains. It is now generally agreed that Freudenberg's view of the biosynthesis of lignin from coniferin via the condensation of monomeric units of the structure

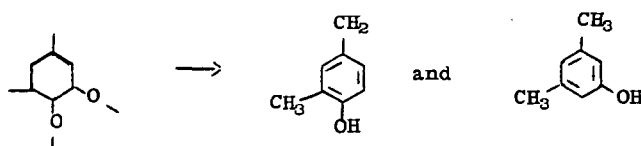


is probably correct, and although the structure of lignin has not been finally clarified, the production, on pyrolysis of fossilised lignin, of a unit having the structure V is not difficult to envisage.

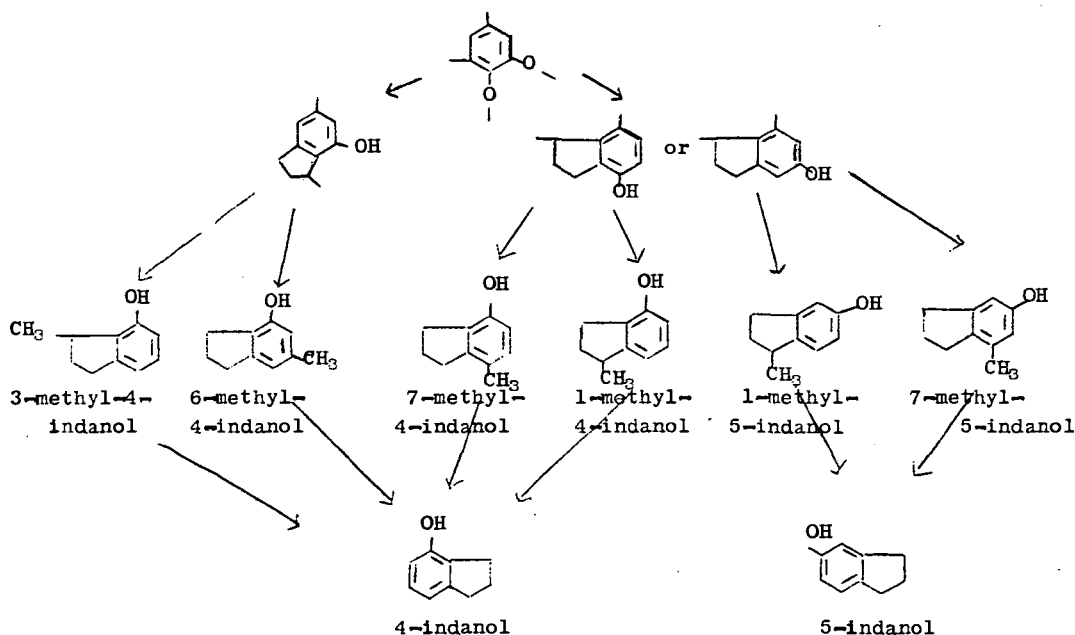


The isomeric distribution of the xylenes and cresols in high-temperature tars is as expected from thermodynamic considerations with the meta compound predominating but in the xylenols the observed distribution in continuous

vertical retort tar differs from what would be expected from either thermodynamic or kinetic considerations. Thus the observed distribution is 33% 2,4-xyleneol, 31% 3,5-xyleneol, 12% 2,6-xyleneol and between 7-9% of each of the 2,3-, 2,5- and 3,4-isomers. The thermodynamic distribution should give almost equal amounts of the 2,4-, 2,5- and 3,5-isomers while from kinetic considerations the 2,4- and 3,4-isomers would be expected to predominate. Shortening of the side-chains and loss of one or other of the oxygen containing groups would yield 2,4-xyleneol or 3,5-xyleneol from the proposed coal degradation product:-

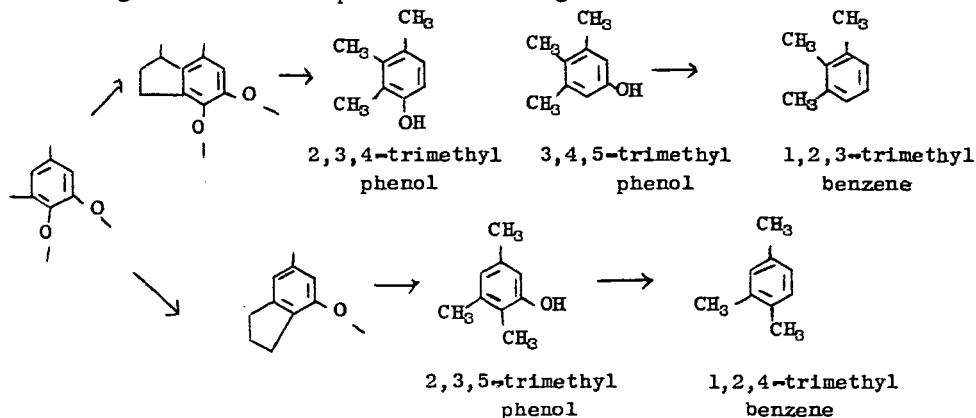


In the higher boiling tar acids from both low-temperature and high-temperature tars, 4-indanol and 5-indanol and their monomethyl derivatives predominate. These can be regarded as derived from the postulated progenitor thus:-

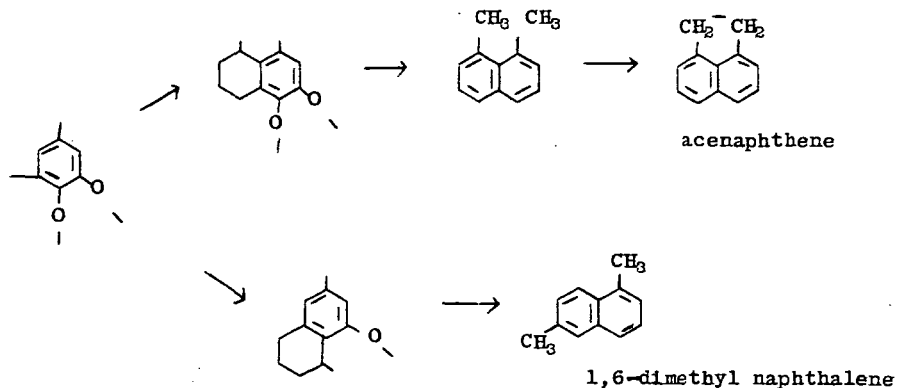


The distribution of the isomeric methyl indanols found in vertical retort tar is 18 parts 7-methyl-5-indanol: 12 parts 3-methyl-4-indanol: 8 parts each of 6-methyl-4-indanol, 7-methyl-4-indanol and 1-methyl-5-indanol: 6 parts of 3-methyl-5-indanol: 1 part each of 4-methyl-5-indanol and 6-methyl-5-indanol. It will be seen that this distribution, except for the absence of 1-methyl-4-indanol, is in conformity with the above scheme.

The trimethyl phenols found in vertical retort tars are restricted to the three isomers 2,3,4-trimethyl phenol, 2,3,5-trimethyl phenol and 3,4,5-trimethyl phenol. Also the isomeric distribution of the three trimethyl benzenes in tar is in the order 1,2,3 > 1,2,4 > 1,3,5 whereas both the thermodynamic and kinetic distributions would predict 1,2,4 > 1,3,5 > 1,2,3. The following scheme would explain these divergencies.



If ring closure yields six-membered rings the predominant products would be expected to be acenaphthene and 1,6-dimethyl naphthalene.



whereas experimental thermodynamic evidence favours the 2,6- and 2,7-isomers as the predominant forms. The analyses of the 250-300°C fractions of continuous vertical retort tar give the ratio of acenaphthene and dimethyl naphthalenes as acenaphthene 1.0, 1,6-dimethyl naphthalene 0.44, 2,6- and 2,7-dimethyl naphthalenes 0.35, 1,7-dimethyl naphthalene 0.19, 2,3-dimethyl naphthalene 0.16 and 1,5-dimethyl naphthalene 0.14.

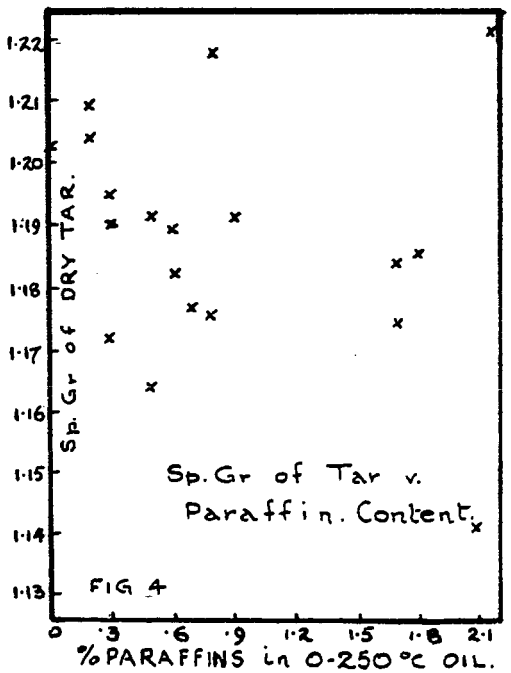
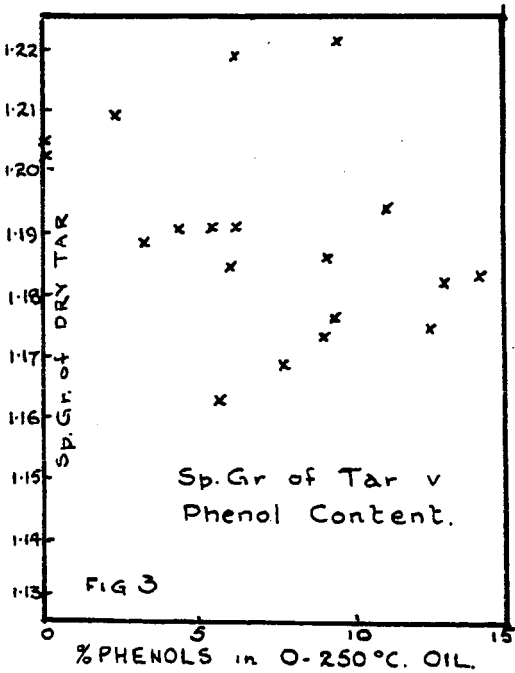
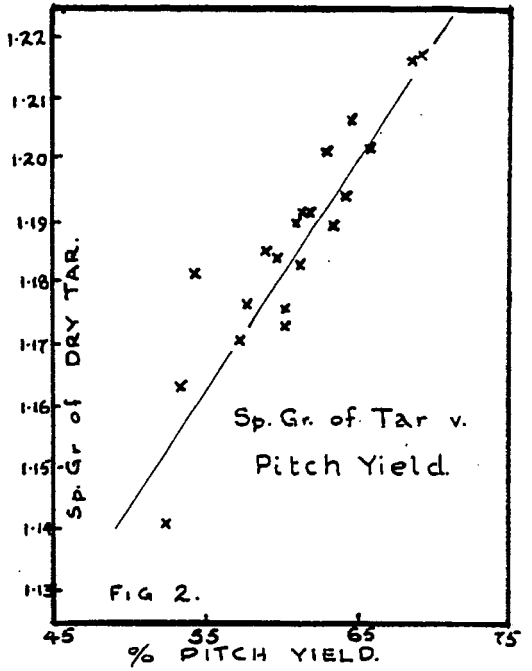
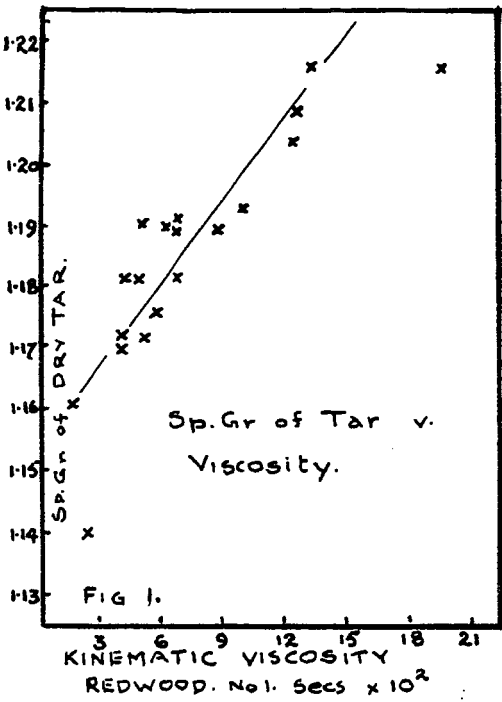
It is appreciated that the evidence from the isomer ratios of tar components for a common precursor derived directly from the coal structure is very flimsy but it seems an interesting speculation and it is in this sense that it is mentioned in this paper. As more reliable data accumulate on the fine structure of tar fractions, particularly those from primary and low temperature tars, and better data become available, either from calculations or experiments of the thermodynamic distribution and kinetic distribution of isomers at the carbonisation temperatures, it should be possible to provide stronger evidence for or against this hypothesis. This possible approach to the problem of the chemical structure of coal should not be ignored.

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PRESENTLY LITTLE-USED BUT POTENTIALLY IMPORTANT
COAL TAR CHEMICALS

113.

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To date, about 400 of the myriad substances contained in coal tar have been definitely identified. This figure may seem small compared to the 10,000 estimated to be in tar but it probably includes all the components that will be used commercially as such since some of the constituents are present in extremely small amounts. The compounds which have been identified are either those which are present in the largest amounts or those which are relatively easy to isolate. It should be remembered that the composition of the lower boiling fractions is more completely understood than is that of the higher boiling fractions and of coal tar pitch--the distillation residue.

The composition of coal tar varies greatly. It is influenced by the type of coking coal employed, by the coking process and by the coking temperature. Further, tar undergoes certain changes in composition on distillation and the yield of various constituents is influenced by the distillation process used.

The development of gas chromatography has greatly facilitated the quantitative determination of coal tar constituents. It proved to be an almost ideal method of investigating tar and its fractions, and has generally superseded other analytical methods that were less accurate and more tedious. The following quantitative data on the occurrence of compounds in coal tar were largely obtained with the aid of gas chromatography. It should be noted that these data relate to high-temperature tar from soft coal of the Ruhr area processed by continuous vacuum distillation.

Figure 1 is a gas chromatogram of such tar. The individual peaks represent the most important constituents from indene (boiling point at one atmosphere: 183.1°C) to coronene (boiling point at one atmosphere: 525°C) in the order of their boiling ranges. As this is a schematic diagram covering the whole tar, not all the quantitatively important compounds are indicated by separate peaks. For instance, the peaks of 1- and 2-methylnaphthalene and also those of phenanthrene and anthracene coincide. A more detailed gas chromatographical analysis of the tar would separate these isomers. However, since gas chromatograms become less easily followed as the number of peaks increases, further diagrams will not be shown.

All together, the compounds identified to date make up about 55 per cent of the tar. In addition, tar contains about 2 per cent of relatively high-molecular-weight, soot-like compounds that cannot be dissolved or distilled--making it impossible to determine their composition by chemical methods. Thus it is apparent that only a small per cent of the number of compounds believed to be present in coal tar have been identified; those that have been identified represent a very significant portion of the tar.

According to present knowledge, a maximum of eleven compounds occur in coal tar in proportions greater than 1 per cent. Excepting the two methylnaphthalenes, all of them are unsubstituted, aromatic substances without functional groups. The three compounds present in the largest proportions are a binuclear, a trinuclear, and a quadrinuclear hydrocarbon.

Table I
Compounds Present in Coal Tar in Amounts
Greater Than 1 Per Cent

<u>Compound</u>	<u>Per Cent</u>
Naphthalene	10
Phenanthrene	5
Fluoranthene	3.3
Pyrene	2.1
Fluorene	2.0
Chrysene	2.0
Anthracene	1.8
Carbazole	1.5
2-Methylnaphthalene	1.4
Dibenzofuran	1.0
1-Methylnaphthalene	1.0

Until quite recently coal tar has been the only source of aromatic compounds. The slight extent to which this source has been exploited, however, is not widely known. Of the eleven most abundant constituents of coal tar, only two--naphthalene and anthracene--are being used on large scale as pure products for chemical processes. Contrasted with naphthalene, almost all of which is recovered and further processed, anthracene is used only to a limited extent in the chemical industry, although the amount has increased recently. This paper is not concerned, however, with compounds now used technically on a relatively large scale, but with the still untapped possibilities of coal tar. What coal tar constituents have been used widely in their pure form? Compared to the potential, the number is extremely small: besides naphthalene and anthracene, the list includes only phenol and its homologs (cresols and xylenols); pyridine and its homologs; and quinoline. With both phenol and pyridine homologs, mixtures and not pure products are frequently used. Nevertheless, it should not be concluded that little attempt has been made over the years to exploit the chemical potentiality of tar.

Most organic industrial processes for the manufacture of synthetic fibers, resins, pesticides, dyestuffs, drugs, etc. employ small, reactive building blocks from which the end products are synthesized. When coal tar components are small and reactive, as phenol and the pyridine bases, they meet these requirements and are used. But most of the compounds present in coal tar have relatively large molecules without functional groups and are quite inert chemically. This is why--what seems surprising at first glance--of the eleven most abundant constituents of coal tar, only two find wide application. Naphthalene, the chief constituent, is a noteworthy exception among the tar aromatics. It has become a valuable raw material because, fortunately, it can be oxidized in high yield to phthalic anhydride.

Conditions may seem less favorable when we consider the other aromatics, but it nevertheless would seem advisable to investigate the various possibilities offered by these raw materials which are available in such quantity. Certainly in recent years remarkable progress has been made in recovery techniques, so that today most of the products are available in purer grades and at lower prices than a few

years ago. Although this has led to a gratifying increase in sales, there is still no realistic comparison between the demand for most products and the quantities that could be produced.

Phenanthrene

Phenanthrene, the second largest constituent of coal tar, still has not been used to any appreciable extent though the phenanthrene skeleton underlies multitudinous hydroaromatic compounds widely distributed in nature and having great physiological significance. These natural products include: resin acids, morphine, sterols, bile acids, digitalis glycosides, sex hormones, and antirachitic vitamins.

There is an extensive literature on the chemical reactions of phenanthrene--such as halogenation, nitration, sulfonation, alkylation, chloromethylation, metalization, hydrogenation, and oxidation--with numerous uses proposed for the reaction products. Uses such as in the manufacture of resins, dyestuffs, drugs, plasticizers, and--as solid chlorination products--nonflammable electrical insulators and impregnants.

About 10 million tons of crude tar are distilled annually in the Western World. Assuming that this entire output has the same phenanthrene content as coal tar from the Ruhr area, or 5 per cent, and that about half of the phenanthrene could be recovered, the impressive quantity of 250,000 tons of phenanthrene yearly would be available. Separation on a large scale would, of course, result in lower production costs. Since phenanthrene has a higher boiling point than naphthalene and because it is more difficult to recover, it will always be more expensive, but if produced on the same scale as naphthalene, its price would be much lower than it is at the present time.

By analogy to naphthalene, it may be expected that phenanthrene can be oxidized to produce a bivalent acid, diphenic acid, which if cheap enough could be used in the manufacture of synthetic resins and plasticizers.

Diphenic acid is already being produced from phenanthrene, but so far there has been no success in developing a simple commercial process with a high yield for the conversion of phenanthrene into diphenic acid or its anhydride. The process currently followed gives not only diphenic acid but also considerable amounts of other oxidation products. Because of the poor yield and trouble with subsequent purification, diphenic acid is currently priced so high that it is used only for specialized purposes. However, much research is going into the problem, so there are good prospects that an economic process will be developed before long. As soon as one application of phenanthrene gains industrial importance, the price reduction will open up additional markets where phenanthrene has been unable to compete for price reasons.

Fluoranthene

While it is well known that large amounts of phenanthrene are available from coal tar, we seem to be less prone to realize that next to naphthalene and phenanthrene, fluoranthene is the most abundant coal tar constituent. Assuming the

conditions described for phenanthrene recovery, fluoranthene is available in the amount of 165,000 tons yearly as a raw material. The fact that organic chemistry treatises frequently ignore fluoranthene entirely or mention it only in marginal notes, shows how neglected the compound has been. Nevertheless, fluoranthene has an advantage over phenanthrene since, like naphthalene, it can be readily obtained from the appropriate fraction in a high purity, because the fluoranthene fraction has no significant content of material less soluble than fluoranthene or which forms mixed crystals with it.

Thus fluoranthene is offered in technical grade in a purity of 97-98%. As with phenanthrene, mass production could reduce its price considerably.

Coal tar is now usually processed by continuous distillation. The fractions recovered, in the order of their boiling ranges, are: water, light oil, middle oil (carbolic oil), naphthalene oil, wash oil, low-boiling anthracene oil, high-boiling anthracene oil, and pitch (distillation residue). Other closely cut distillate fractions yielding concentrates of other main constituents could be separated in the same way as the naphthalene fraction in the primary distillation. However, since the largest part of coal tar distillate is used as creosote, a broad complicated mixture of compounds, this type of distillation is not profitable or generally practiced.

Fluoranthene is a constituent of the high-boiling anthracene oil, and to a lesser extent of the pitch. To obtain the fluoranthene fraction, the high-boiling anthracene oil must be distilled further. This yields a number of other fractions, the most important one being the pyrene (boiling points at one atmosphere: pyrene, 393°C; fluoranthene, 383.5°C). Fluoranthene costs would be much lower if the pyrene fraction could also be used instead of being returned to the high boiling anthracene oil. (The co-product problem becomes more complex and important as the amount of the desired material in the tar becomes less. In practice, only the two most abundant constituents, naphthalene and phenanthrene, are free of this burden).

Compared to phenanthrene, the literature on the chemical reactions of fluoranthene is limited. Halogenation, nitration, sulfonation, hydrogenation, oxidation, and condensation with phthalic anhydride and acid chlorides are reported. Despite the symmetry of its molecule, fluoranthene is not chemically inert! Since fluoranthene is readily accessible in a high purity and is relatively reactive, why has it had no important practical application to date? Probably because the compound failed to attract the attention of chemists in the past and since the ease of its recovery was not fully appreciated. An examination of its reactions suggests fluoranthene could perhaps be used as a starting point for the synthesis of drugs and particularly of dyestuffs.

The price of fluoranthene would be the determining factor in the commercialization of any dye derived from it and the price could be reduced only if a certain minimum sales outlet were assured. As far as we know at the present time the oxidation type reactions are not as promising as with naphthalene or phenanthrene because no novel multicarboxylic acids have been made from it.

Pyrene

Unlike phenanthrene and fluoranthene, pyrene is already being used as a raw material on a very modest scale compared to the potential 100,000 tons a year which is available. The chemistry of pyrene has been extensively investigated (halogenation, nitration, hydrogenation, oxidation, sulfonation, condensation, etc.) A large number of condensation reactions have been reported and deserve special mention. These include not only condensation with phthalic anhydride but also with acetic anhydride, benzoyl chloride, diazoacetic ester, dichlorodiphenylmethane, glycerin, cyanuric chloride, and formylmethylaniline.

The possibility of combining the production of fluoranthene and pyrene (boiling points at one atmosphere: fluoranthene, 383.5°C; pyrene, 393.5°C) has already been discussed under fluoranthene. As in the case of fluoranthene, pyrene is found in both the high-boiling anthracene oil and pitch. However, recovery of pyrene is more complicated because its fraction has some slightly soluble components boiling close to pyrene, including 1,2-benzodiphenylene oxide and 2,3-benzodiphenylene oxide. These are troublesome and expensive to remove. This explains the fact that pyrene is not ordinarily offered in as high a purity as fluoranthene. The technical grades available have a pyrene content of only 90-95%.

It is difficult to forecast if pyrene, so far used mainly as a starting material for the synthesis of dyestuffs, will become important in other fields. With successful utilization of fluoranthene as a chemical raw material, the market outlook for pyrene would undoubtedly improve. Many possibilities for its use are currently barred by its high price. Even if pyrene and fluoranthene recovery are combined, however, pyrene production costs would be reduced only slightly because, as previously mentioned, it is harder to upgrade the pyrene fraction than the fluoranthene fraction.

Like phenanthrene, there are interesting oxidation products of pyrene, such as 4,5-phenanthrenedicarboxylic acid and 1,4,5,8-naphthalenetetracarboxylic acid.

Naphthalenetetracarboxylic acid would be a particularly promising pyrene derivative if there were a simple oxidation process available giving a high yield of the acid. Experiments directed to this end have not yet given reason for optimism.

Fluorene

Wash oil boils between 230°C and 300°C; fluorene, occurring in tar in about the same proportion as pyrene, has the highest boiling point of main constituents in this fraction. Acenaphthene and dibenzofuran (diphenylene oxide) boil slightly below fluorene (boiling points at one atmosphere: acenaphthene, 278.2°C; dibenzofuran, 285.1°C; fluorene, 297.9°C). It is, therefore, convenient to consider the three together. However, fluorene and dibenzofuran must be carefully separated by distillation because they form a continuous series of solid solutions which, of course, cannot be separated by crystallization techniques.

Formation of mixed crystals is common among the constituents of coal tar. Phenanthrene and anthracene, phenanthrene and carbazole, and chrysene and 1,2-

benzanthracene are other quantitatively important compounds which form a continuous series of mixed crystals characterized by a curve having no maximum or minimum between the freezing points of the pure components. The formation of mixed crystals between phenanthrene, anthracene and carbazole is the main reason that phenanthrene is more difficult to purify than naphthalene.

Fluorene is the first of the coal tar constituents discussed so far to have a reactive group: in this case the methylene group between the two benzene rings has highly reactive hydrogen atoms. In spite of numerous reactions described in the literature and numerous uses suggested, such as the manufacture of cleaning and wetting agents, textile auxiliaries, pharmaceuticals, disinfectants, pesticides, dyestuffs, liquid scintillators, and thermoplastic resins, all attempts to promote widescale development of fluorene as a chemical raw material have been unfruitful to date. Recent developments indicate that there may be an outlet in drug synthesis because pharmacological substances currently being tested have been obtained from fluorenone, a product readily prepared from fluorene.

Chrysene

Chrysene, the most abundant constituent of coal tar pitch, is also found in smaller amounts in high-boiling anthracene oil. Because of a high-boiling point (440.7°C at one atmosphere) and the extraordinarily high-melting point (255°C), the product is hard to recover in its pure form. The starting point for chrysene production is usually the distillate from the manufacture of hard pitch, though pitch coke oil from the coking of hard pitch is also rich in chrysene.

Provided that suitable applications can be found, there seems to be no reason why all of the compounds discussed up to this point should not be used on large scale industrially. There is, however, less chance for chrysene despite the fact that its occurrence in coal tar is about the same as that of fluorene and pyrene. Purification of chrysene is more difficult and the higher cost of the compound will be a serious handicap to its broad utilization. Chrysene derivatives have been used to some extent in ultraviolet filters and sensitizers.

Carbazole

Carbazole, quantitatively the most important heterocyclic constituent of tar was, until recently, sold in large quantities. It is recovered as a co-product in anthracene purification. It was used for the production of dyestuffs and pesticides.

When fused with polysulfide in butanol or roasted with polysulfide in the presence of organic bases such as benzidine, the 3-(4'-hydroxyphenyl)-aminocarbazoles obtained by the condensation of carbazole with p-nitrosophenol yield the sulfur dyestuff, hydron blue R, or when N-ethylcarbazole is employed, hydron blue G. 2-Hydroxycarbazole-3-carboxylic-acid-p-chloroanilide has become familiar as the brown dyestuff, naphthol AS-LB. 1,3,6,8-Tetranitrocarbazole became important as an insecticide under the trade name, Nirozan.

Finally, through the production of poly-N-vinylcarbazole a plastic has been developed from carbazole having good dielectric properties, good chemical resistance, high softening point, and thermal stability. This product has found commercial use in the electrical industry (trade names for polyvinylcarbazole: Luvican and Polectron).

Unfortunately, the use of all these interesting derivatives has declined considerably in recent years, and some manufacturers of dyestuffs now specify that the anthracene material supplied to them contain less than a certain amount of carbazole.

A prognosis of the market for carbazole is, therefore, difficult. There is reason for certain optimism about the future of carbazole because it is a co-product in the production of anthracene and it does have a number of significant uses. Nevertheless, carbazole sales can be restored only with the development of new uses.

1-Methylnaphthalene/2-Methylnaphthalene

The two monomethylnaphthalenes are present in tar in very considerable amounts, with 2-methylnaphthalene predominant. In high-temperature tar, the ratio of naphthalene to the monomethylnaphthalenes is about 4:1, the lower the coking temperature, the more this ratio shifts in favor of the methyl- and dimethylnaphthalenes.

The methylnaphthalene fraction is a constituent of the "wash oil". It is distilled after the naphthalene fraction before diphenyl and the dimethylnaphthalenes. Methylnaphthalene production, therefore, fits nicely into recovery of the other three.

Because of their ready accessibility the methylnaphthalenes have become more important recently, even though the quantities sold are still very limited. Many possible uses have been proposed for each isomer; but these frequently overlap uses for naphthalene. Since naphthalene is cheaper, it has an advantage over the monomethylnaphthalenes in these cases. The syntheses of 1-naphthylacetic acid serves to illustrate such competition between naphthalene and 1-methylnaphthalene. 1-Naphthylacetic acid, used as a growth promoter, can be made from 1-methylnaphthalene by chlorination, reaction with KCN and subsequent hydrolysis. It can also be made by the chloromethylation of naphthalene followed by the same reactions. The synthesis selected then becomes a matter of cost.

1-Methylnaphthalene has an unusually low freezing point (-30.6°C) which is lowered further in the technical grade by the presence of isomeric 2-methylnaphthalene. Because of this property and its high solvent power, the alpha isomer is used as a solvent and as a heat transfer oil. It can also be used as a carrier in the dyeing of polyester fibers, as a cetane-number indicator. It has been used for determining the theoretical number of trays in distillation columns. Other suggestions for use are as an extraction agent for sulfur, as a constituent of liquid dielectrics, and as a starting material in the manufacture of plasticizers, pesticides, plastics, and textile auxiliaries. However, these suggestions have not been developed to any significant extent.

The numerous uses which have been proposed for 2-methylnaphthalene, include the production of dyestuffs, textile auxiliaries, growth inhibitors, detergents, emulsifiers, and wetting agents. The beta isomer is of importance in that its 1,4-quinone is a starting product for the manufacture of Vitamin K.

Dibenzofuran (Diphenylene Oxide)

Dibenzofuran is the most abundant oxygen heterocyclic compound in coal tar. The analogy in composition and occurrence between dibenzofuran and carbazole, the most important nitrogen heterocyclic, is striking. The presence of dibenzofuran in the wash oil and the advantages of combining its production with that of fluorene and acenaphthene have already been discussed.

Dibenzofuran is the skeletal substance of morphine. The reactions of dibenzofuran (halogenation, nitration, sulfonation, methylation, hydrogenation, and condensation) are reported in the literature. Possible uses are also described, such as the manufacture of disinfectants, insecticides, wood and other types of preservatives, textile auxiliaries, synthetic resins, high-temperature lubricants, dyestuffs, and additives for candle mixes. Dibenzofuran has been used to some extent as a dyestuff intermediate. Because of its high thermal stability, the product is suitable for heat transfer media although its high melting point (+82°C) is an objection.

An interesting derivative of dibenzofuran is o,o'-biphenol (2,2'-dihydroxydiphenyl), obtained by fusion with caustic potash. This compound is used in the manufacture of disinfectants and pesticides.

Acenaphthene

The acenaphthene content of crude tar is about 0.5%. However, larger quantities may be found in coal tar distillates because acenaphthene is one of those few compounds which may be formed in tar during distillation. The amount formed in this way may be equal to that originally present and the net acenaphthene content of coal tar is about 1%, roughly the same as dibenzofuran. Like fluoranthene it is easily purified by crystallization of the appropriate distillation fraction and the technical grade is usually 97-98% pure.

The chemical reactions which result in the production of secondary acenaphthene are not completely understood. The most likely reaction would be the dehydrogenation of 1,8-dimethylnaphthalene but since this cannot be demonstrated quantitatively, it must be assumed that there are other compounds in coal tar which are converted to acenaphthene by heat.

Like pyrene, acenaphthene belongs to the class of aromatics that have been used as starting materials for dyestuffs, but on a scale which consumes only a fraction of that which could be produced.

By means of catalytic gas-phase dehydrogenation, acenaphthene can be converted to acenaphthylene, which can be easily polymerized with peroxide catalysts. Like co-polymers containing acenaphthylene, the polyacenaphthylenes are noted

chiefly for their good electrical properties and high melting points but have not yet attained practical importance. A high yield of naphthalic anhydride is obtained from acenaphthene by catalytic gas-phase oxidation. Naphthalic anhydride has been used chiefly in the manufacture of dyestuffs. At a lower price it could probably be used for the production of synthetic resins.

On the whole, the market outlook for acenaphthene is more favorable than for its two by-products, dibenzofuran and fluorene. To reduce production costs as far as possible, effort must be concentrated on finding uses for substantial quantities of all three compounds.

Indene

Indene, the lowest-boiling of the most abundant coal tar constituents, is the reverse of acenaphthene so far as recoverability is concerned. The primary indene content of tar is almost 1 per cent. But in counter-distinction to acenaphthene, the amount of which increases during distillation, the amount of indene is decreased because at high temperatures and in the presence of hydrogen it is easily converted into indan. The extent to which the indene content is reduced and indan formed depends on the type of distillation process; the longer and higher the temperature at which the tar containing indene is heated, the greater the reduction of indene content. Under unfavorable conditions, more than 50 per cent of the original indene content of the tar may be lost. Since indene is more valuable than indan because of its higher reactivity, the hydrogenation of indene is an extremely undersirable reaction.

Indene cannot be classed as one of those coal tar constituents which has no practical use at this time even though it is not isolated and used as such. Indene is the principal constituent of coumarone resins. These would more accurately be called indene resins.

Because of its relatively high freezing point--(-1.6°C) pure indene can be prepared from the appropriate distillation fraction by extreme cooling. However, in spite of the many uses proposed for it, pure indene is not important commercially.

In addition to the large volume constituents of coal tar so far discussed, there are many other materials available in reasonably large amounts, which likewise have not attained commercial significance. The most important of these appear in the following table.

Table II
Important Coal Tar Constituents

<u>Compound</u>	<u>Content of Coal Tar (Per Cent)</u>
Diphenyl	0.4
Indole	0.2
2-Phenylnaphthalene	0.3
Isoquinoline	0.2
Quinaldine	0.2
Acridine	0.6
Phenanthridine	0.2
7,8-Benzoquinoline	0.2
Thianaphthene	0.3
Diphenylene Sulphide	0.3

Diphenyl

The diphenyl-indole fraction occurs between the methyl- and dimethylnaphthalene fractions. Recovery of diphenyl and indole is conveniently combined with the methylnaphthalenes.

Diphenyl is well known as a constituent of heat transfer oils. The eutectic mixture of diphenyl and diphenyloxide is sold under the trade names "Dowtherm A" and "Diphyl".

Diphenyl is also used as a preservative; for example, citrus fruit wrappers are frequently impregnated with diphenyl. It should be mentioned too that diphenyl is the basic substance of the benzidine dyestuffs, though they are normally produced from other starting materials.

Contrasted with what could be produced, very little coal tar diphenyl is used commercially. Coal tar diphenyl is under a handicap because diphenyl is available from other sources. It is obtained as a by-product in the synthesis of phenol by the chlorination process and it can be made by the pyrolysis of benzene. The diphenyl market, therefore, is divided between that recovered from coal tar and that made synthetically.

Indole

Indole, the nitrogen analog of indene, is one of the most interesting constituents of coal tar. Separation of indole and diphenyl is not possible by simple distillation because the two compounds have vapor pressure curves which lie close together and also form an azeotropic mixture. The boiling point of the diphenyl-indole azeotrope is a few degrees lower than the pure products (boiling points at one atmosphere: indole, 254.7°C; diphenyl, 255.6°C). Separation of indole and diphenyl is achieved by taking advantage of the slight acidity of the imide group and isolating the indole from the diphenyl fraction via its potassium compound by fusion with caustic potash. Diphenyl then can be recovered from the indole-free oil by fractionation and crystallization.

Another method of separating the two compounds is by the addition of a third component, diethylene glycol. Azeotropic mixtures of diphenyl-diethylene glycol and indole-diethylene glycol boil twelve degrees apart; under normal pressure they boil at 230.4°C and 242.6°C respectively (uncorrected). In this case, the azeotropic effect is so pronounced that separation by distillation does not require particularly efficient columns.

Indole is used commercially in several fields of chemistry. As might be expected from its occurrence in nature as a constituent of jasmine and orange blossom oils, it has long been used as a perfume fixative. The extraction of indole from coal tar in a state of purity which satisfies the perfume manufacturers is a chemical achievement since even trace amounts of impurity will falsify the aroma.

Indole is a starting material for growth-promoting substances and for amino acids. 3-Indoleacetic acid (indole-3-acetic acid) is one of the first growth-promoters

used. It is known commercially as heteroauxin. One way of making it is by the condensation of indole with formaldehyde and hydrochloric acid followed by condensation with potassium cyanide and hydrolysis of the resulting nitril. Alpha-amino-3-indole-propionic acid, known as tryptophane, is an integral component of many types of protein and one of the vital amino acids. 3-(Dimethylaminomethyl)-indole (gramine), obtained by a Mannich Reaction of indole with formaldehyde and dimethylamine, is an intermediate in the synthesis of tryptophane. Tryptophane is made by reacting gramine with acetaminomalonic ester and subsequent saponification.

Although the quantity of indole used is still small, improvement in the recovery process in recent years has resulted in steadily increased sales. Possibilities for indole are not at all exhausted with the uses mentioned. Interesting intermediates for dyestuffs and drugs can be made by reacting the hydrogen atom attached to the nitrogen. Of course, the relatively small amounts of indole in coal tar and the complicated methods for extracting and purifying it will never permit a price comparable to mass-volume products, but it is hoped that the recent advances in the preparation of indole will lead to a greater use of this interesting compound.

2-Phenylnaphthalene

Unlike indole, 2-phenylnaphthalene is a substance about which little can be said. Recently it was found that this compound, formerly classed among the rare constituents, actually is rather abundant in coal tar and can be recovered in relatively large amounts. The 2-phenylnaphthalene fraction boils below fluoranthene, so its recovery must be combined with that of fluoranthene and pyrene. Since there is no demand, 2-phenylnaphthalene is presently produced only in laboratory quantities. If a demand should develop the methylphenanthrenes, which boil below phenylnaphthalene, would become more accessible. There are considerable quantities of these in tar.

Isoquinoline/Quinaldine

As already mentioned, the only coal tar bases presently being used to any extent commercially are pyridine, pyridine homologues and quinoline. The problem of separating tar bases from their co-products is even greater than in the case of the neutral hydrocarbons. Crude bases are extracted from the appropriate distillation fraction by means of mineral acid from which they are subsequently liberated by the addition of caustic soda. Because of the complex nature of tar, distillation fractions do not contain only the particular tar base desired. Further, the formation of azeotropic mixtures between the hydrocarbons and the tar bases causes the latter to be distributed over a broad distillation range. Thus the extraction process invariably yields fractions which are mixtures of several compounds.

Isoquinoline and quinaldine are the most important compounds which occur with quinoline in the quinoline fraction. Since they boil above quinoline they occur in the distillation residue from which they could be recovered if a demand for them were to develop.

Table III

	<u>B.P. at Atmospheric Pressure - °C</u>
Quinoline	237.3
Isoquinoline	242.8
Quinaldine	246.9

There is extensive literature on the chemical reactions of isoquinoline and quinaldine. Isoquinoline is used as an auxiliary solvent in dyeing and as a starting product in the preparation of isoquinoline red and other cyanine dyestuffs, photographic sensitizers, drugs, pesticides, and vulcanization accelerators. Quinaldine can be used for similar purposes. The most important quinaldine dyestuffs include quinoline yellow, quinoline red, and ethyl red, as well as sensitizing dyes. Quinaldine can also be used as an inhibitor for metals and as a seed disinfectant. Although both these compounds could be produced in considerable volume, none of the uses has reached significant size.

Acridine Phenanthridine 7,8-Benzoquinoline

The three most important and most easily recovered tar bases in anthracene oil are acridine, phenanthridine, and 7,8-benzoquinoline.

Acridine is the best-known and occurs in the largest amount. None of the three bases has as yet been used on large scale, although interest in acridine has been increasing recently.

Acridine is in point of fact the base of numerous dyestuffs and drugs; but acridine dyestuffs are usually manufactured from 1,3-diaminobenzene and aliphatic or aromatic aldehydes. Even the syntheses of such well-known acridine derivatives as the drugs Trypaflavin (3,6-diamino-10-methylacridinium chloride) and Rivanol (2-ethoxy-6,9-diaminoacridine) do not usually involve acridine.

The extent to which 7,8-benzoquinoline occurs in coal tar has only been realized recently. Its only use at the present time is in the separation of meta and para cresol in gas chromatography. As with acridine, several drugs can be derived from phenanthridine; for example, quaternary salts of diaminophenanthridinium series have good trypanocidal properties.

Because of limited demand and the resulting high costs of producing very small batches of these compounds, the prices of acridine, phenanthridine, and 7,8-benzoquinoline are still high. Production on a larger scale--and the amounts of raw material are very adequate for this--would reduce costs considerably.

Thianaphthene Dibenzothiophene (Diphenylene Sulfide)

Thianaphthene and dibenzothiophene are the most abundant sulfur compounds found in coal tar. Thianaphthene is recovered with naphthalene, and the two can be separated only with difficulty because of their close boiling points (boiling points at one atmosphere: naphthalene 217.9°C; thianaphthene, 218.8°C). The formation of mixed crystals further complicates the separation.

The separation of phenanthrene and dibenzothiophene, the sulphur bearing compound that occurs with it, is not as difficult. The difference in boiling points is greater--(331.4°C; phenanthrene 336.5°C) and separation by distillation is more effective. Since dibenzothiophene distills just prior to phenanthrene, the limited market for phenanthrene has restricted the amount of dibenzothiophene recovered.

Both thianaphthene and dibenzothiophene could be recovered from coal tar in substantial amounts but it must be remembered that the cost would be high even if they were recovered on large scale.

Up to the present, very little use has been found for these two compounds. Thianaphthene has been used to some extent in the manufacture of drugs. Other proposed uses are the production of thioindigoid dyestuffs and herbicides from thianaphthene and preservatives with a fungicidal and bactericidal effect from dibenzothiophene. None has practical significance.

Besides the substances which have been discussed there are numerous other compounds that can be obtained from coal tar in relatively large quantities if needed. However, it should be remembered that the recovery and purification problem becomes more complicated as the concentration of the desired compound in the tar decreases. The economics of the processes are affected accordingly.

Attention is drawn to the dimethylnaphthalene fraction, which constitutes about 2 per cent of the tar and lies between the diphenyl and acenaphthene fractions. To date, the following nine dimethylnaphthalenes have been identified in coal tar:

1,2-dimethylnaphthalene	
1,3	"
1,4	"
1,5	"
1,6	"
1,7	"
2,3	"
2,6	"
2,7	"

1,6- and 2,6-Dimethylnaphthalene can be recovered relatively easily, but the isolation of the other compounds is very costly and complicated.

Anthracene oil has two interesting methylhomolog fractions: first, preceding the phenanthrene fraction is the methyl fluorene fraction which accounts for 1.8 per cent of the tar and includes 1-, 2-, 3-, 4-, and 9-methylfluorene; and secondly, following the carbazole fraction, the methylphenanthrene fraction which accounts for 1.8 per cent of the tar and consists mainly of 1-, 2-, 3-, and 9-methylphenanthrene as well as 4,5-methylenephenanthrene. The benzofluorene fraction, being the highest boiling portion of the anthracene oil, also deserves mention. Distilling after the fluoranthene fraction, it accounts for 1.6 per cent of the tar and consists mainly of 1,2-, 2,3-, and 3,4-benzofluorene, as well as 5,12-dihydrotetracene.

The coal tar pitch fractions offer a large reservoir of quadrinuclear and multinuclear aromatics. These need not be discussed because even though some pitch constituents can be recovered in large quantities, their separation is beset by difficulties which would preclude the possibility of cheap production even in volume. Reference has been made already to this problem under the discussion of chrysene.

Bulk tar constituents, with the exception of 1- and 2-methylnaphthalene, are all unsubstituted, binuclear and multinuclear aromatics which include only two heterocyclic compounds, dibenzofuran and carbazole. Special attention has been focused on fluoranthene which up to now has not received adequate attention, despite the fact that next to naphthalene and phenanthrene it is the most abundant constituent of coal tar:

This has been a review of coal tar products which could be made available in substantial quantities if a demand for them were created. The data show that very few aromatics, even those which are readily accessible, are presently used as pure products--or stating this thought in another way--there is a very large source of raw material available which has not yet been exploited.

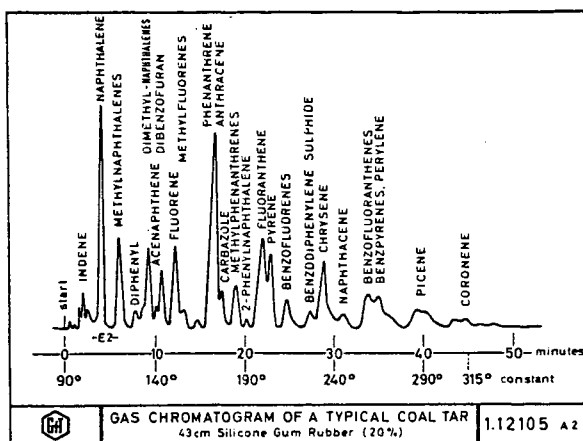


Fig. 1

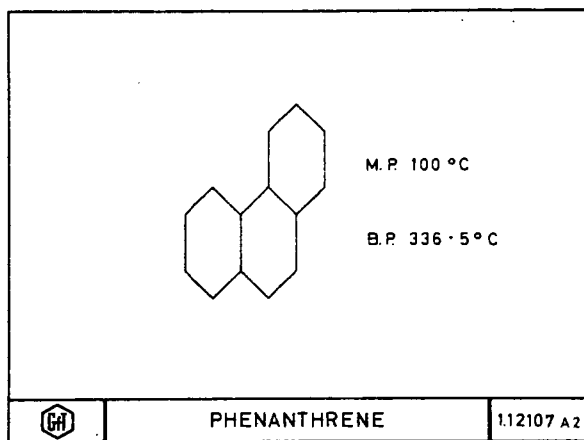


Fig. 2

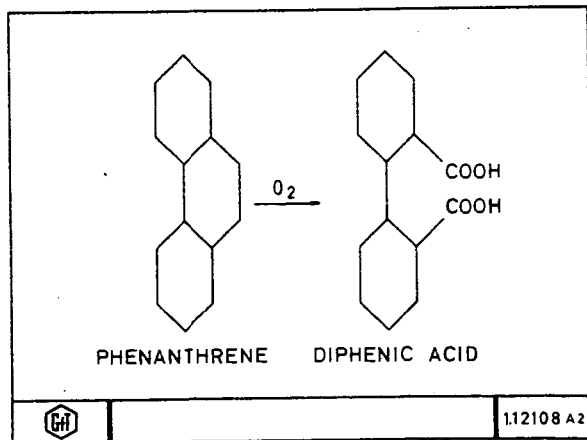


Fig. 3

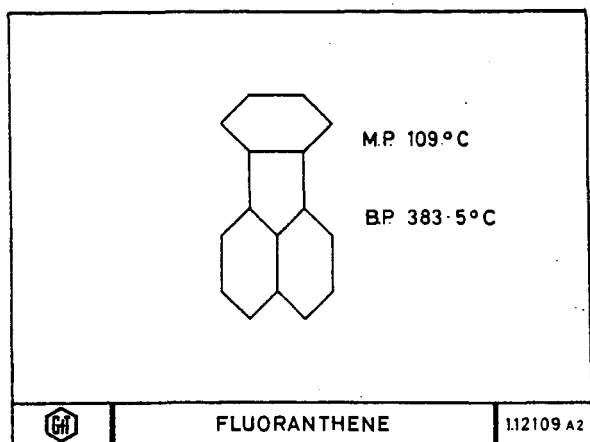


Fig. 4

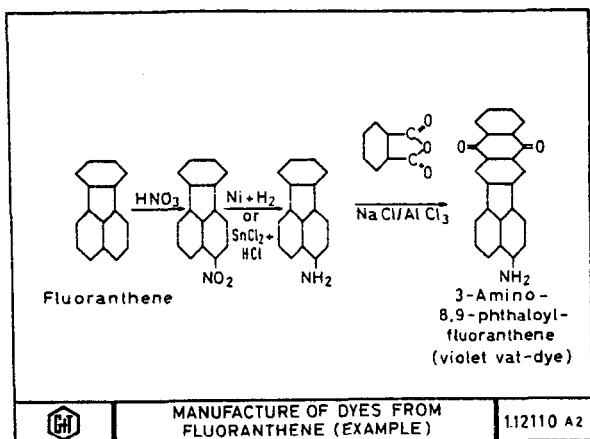


Fig. 5

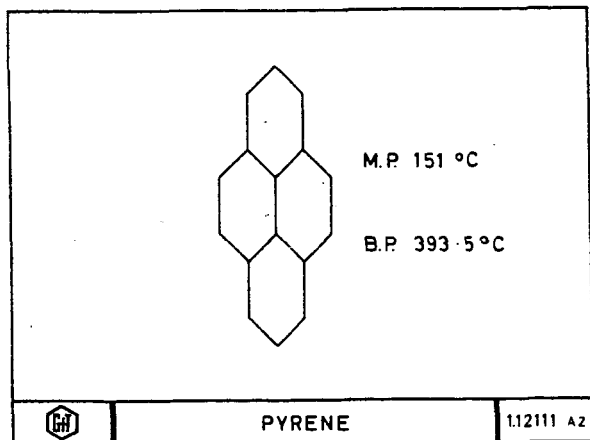


Fig. 6

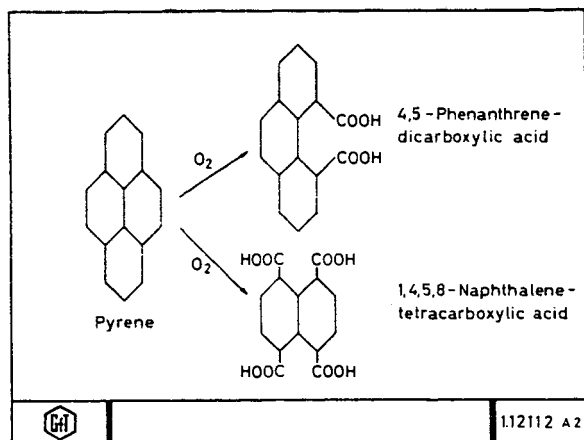


Fig. 7

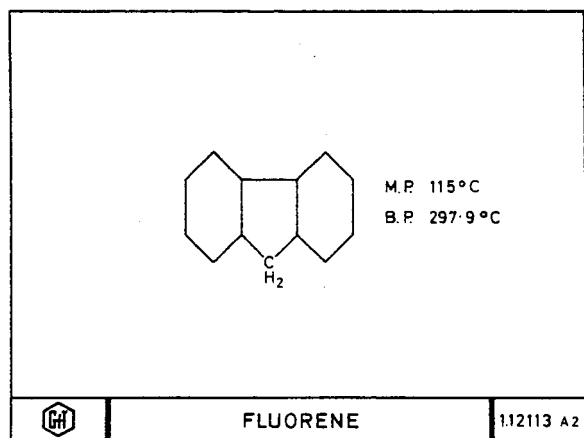


Fig. 8

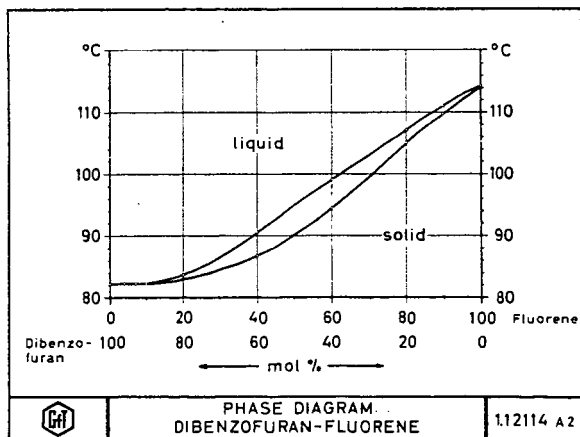


Fig. 9

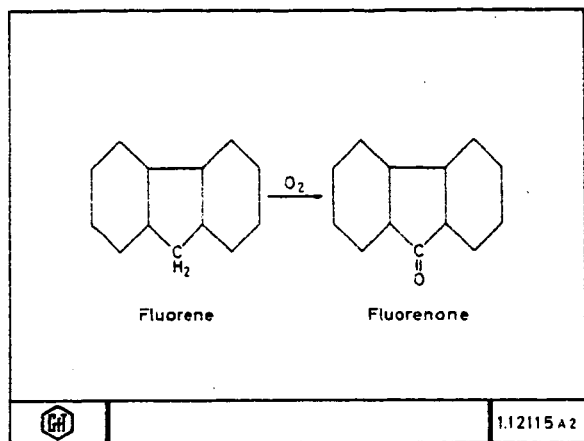


Fig. 10

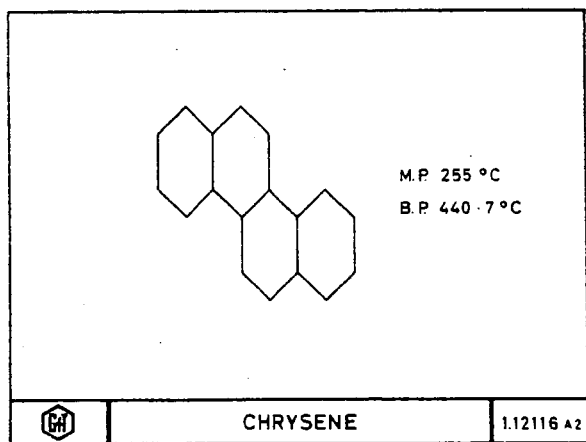


Fig. 11

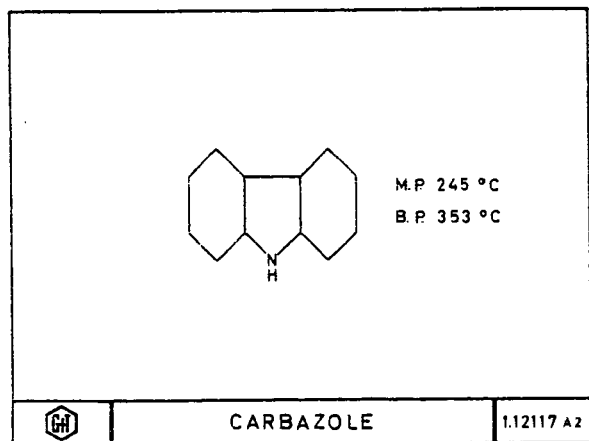


Fig. 12

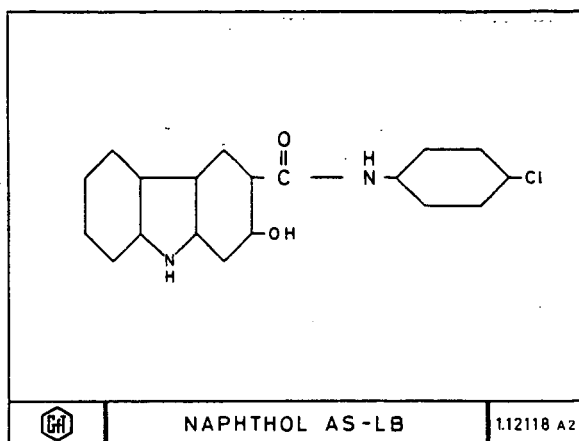


Fig. 13

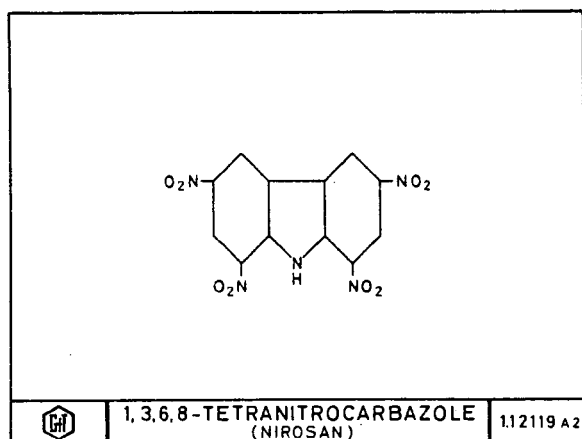


Fig. 14

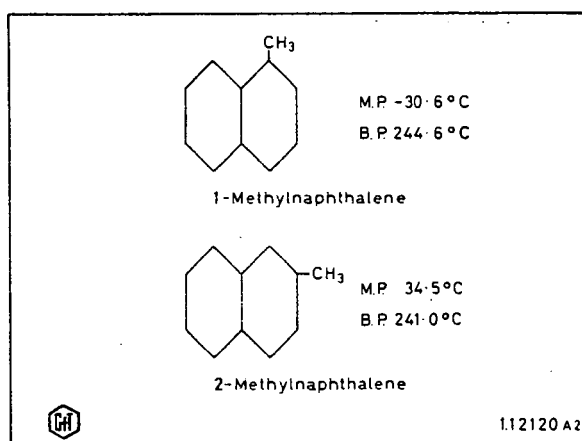


Fig. 15

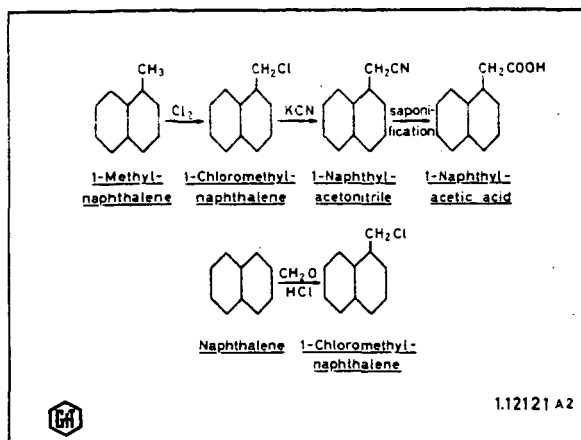


Fig. 16

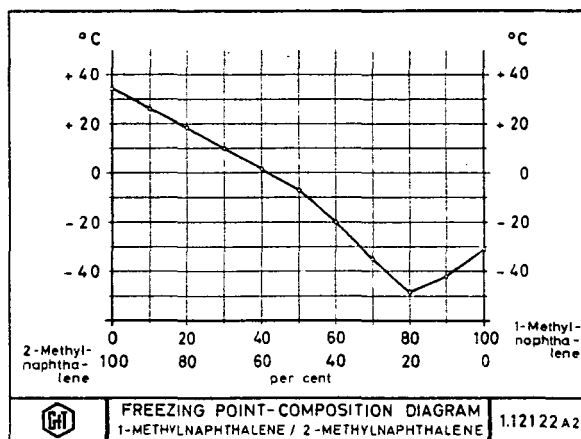


Fig. 17

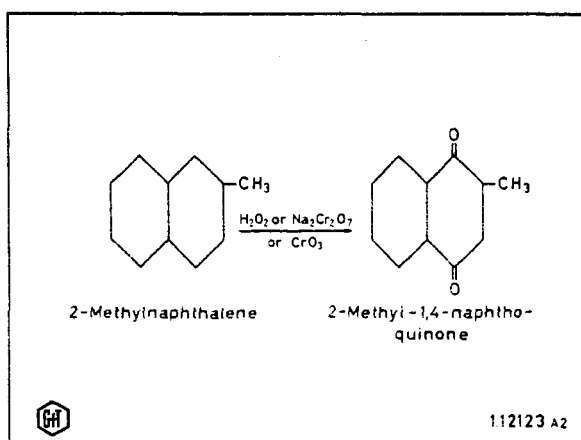


Fig. 18

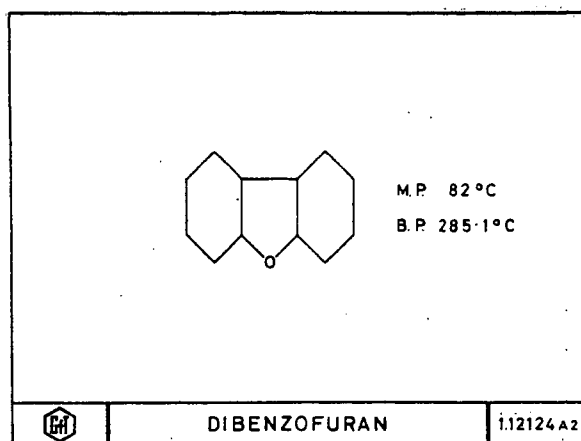


Fig. 19

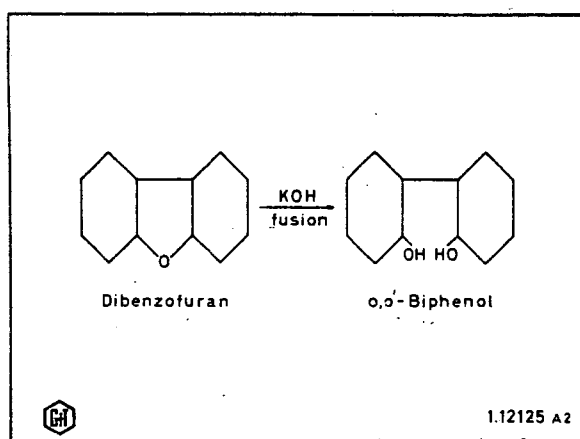


Fig. 20

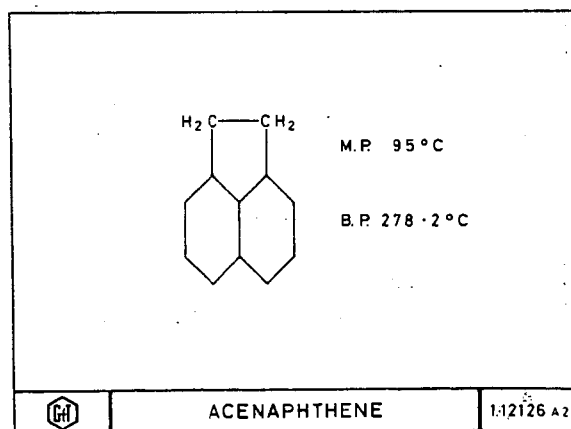


Fig. 21

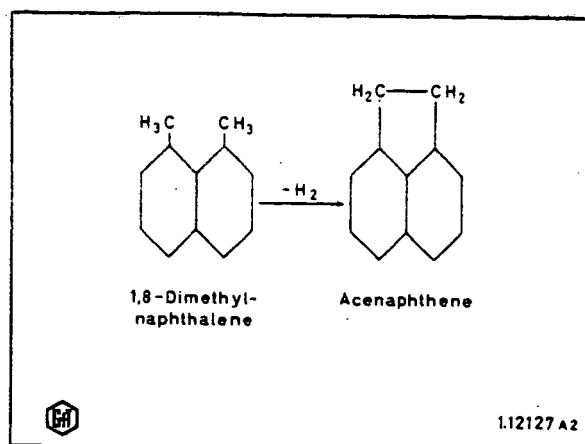


Fig. 22

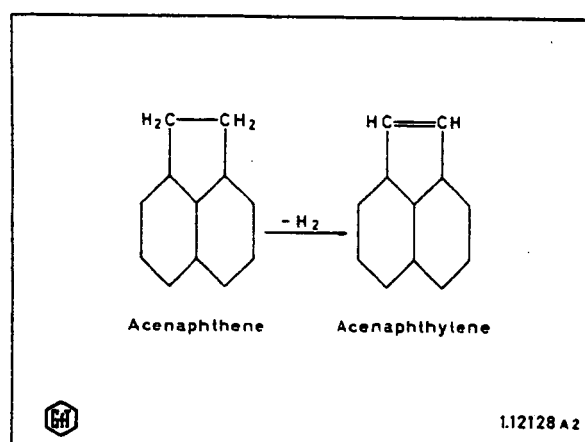


Fig. 23

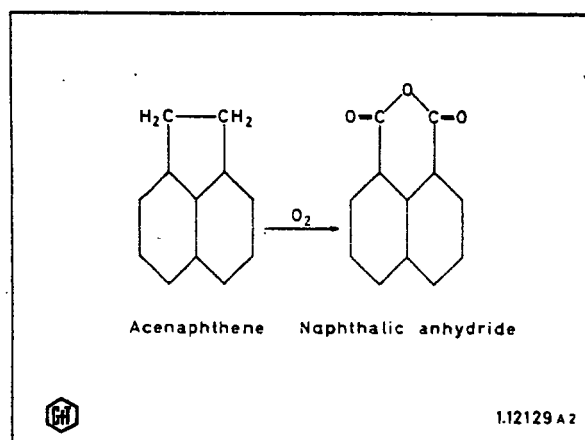


Fig. 24

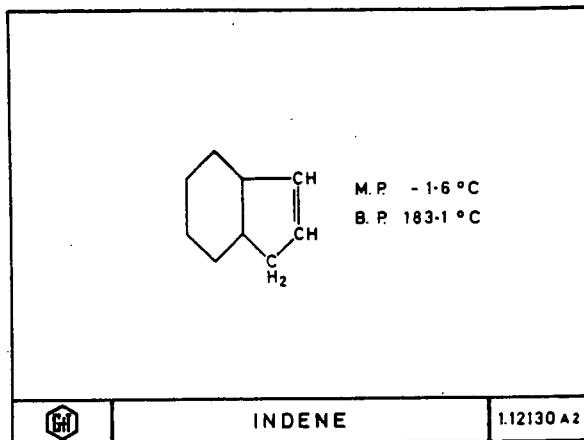


Fig. 25

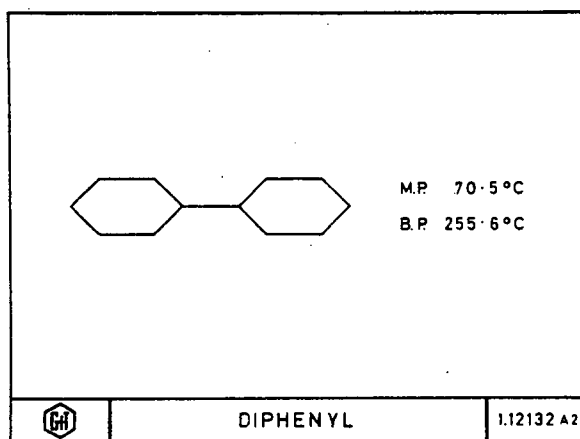


Fig. 26

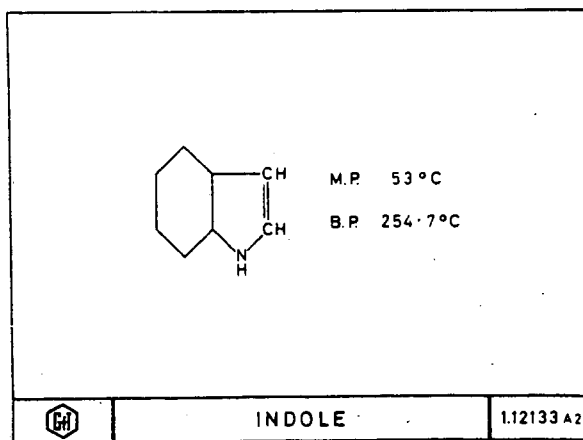


Fig. 27

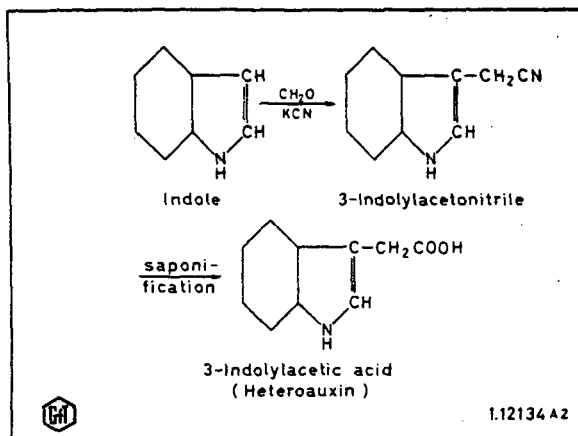


Fig. 28

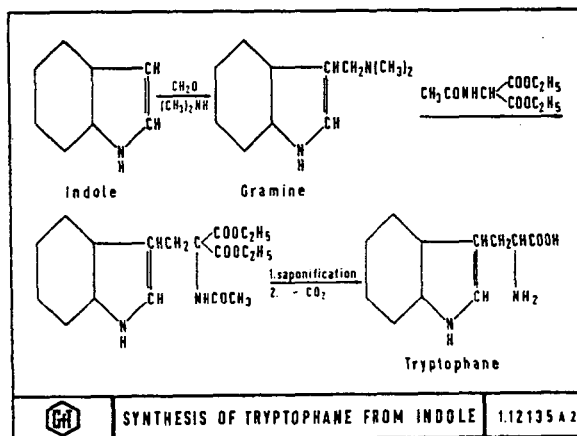


Fig. 29

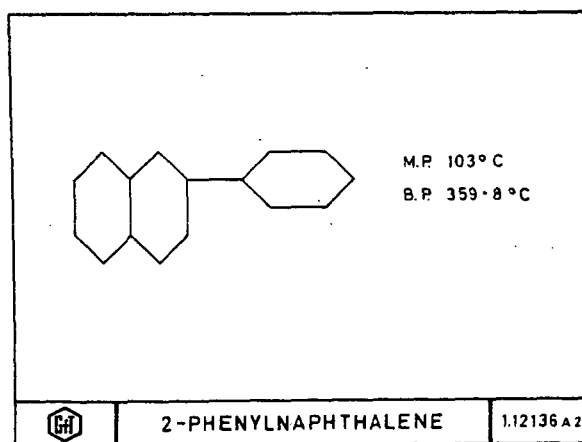


Fig. 30

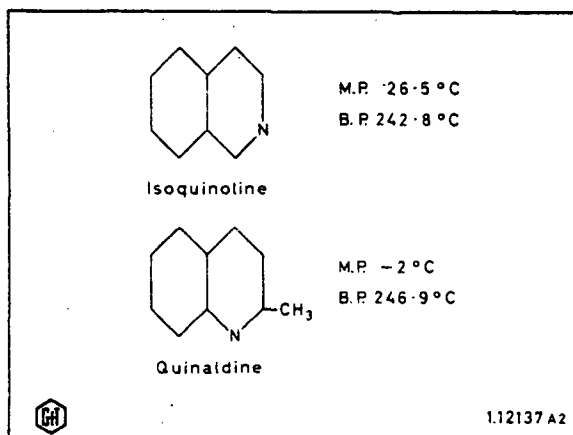


Fig. 31

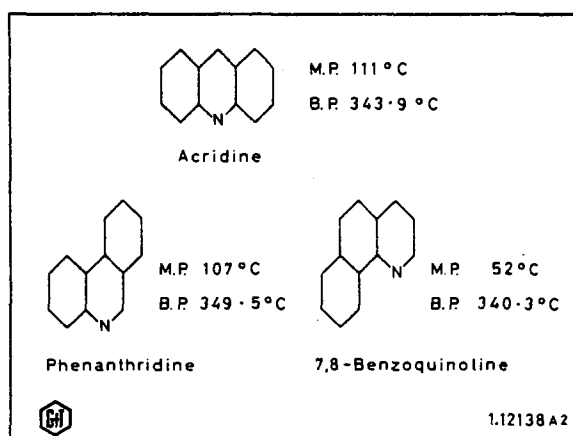


Fig. 32

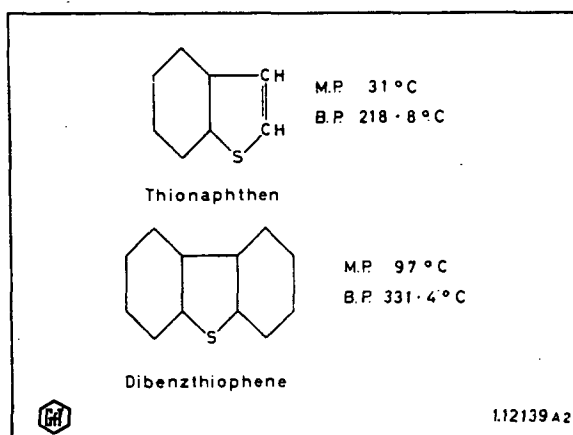


Fig. 33

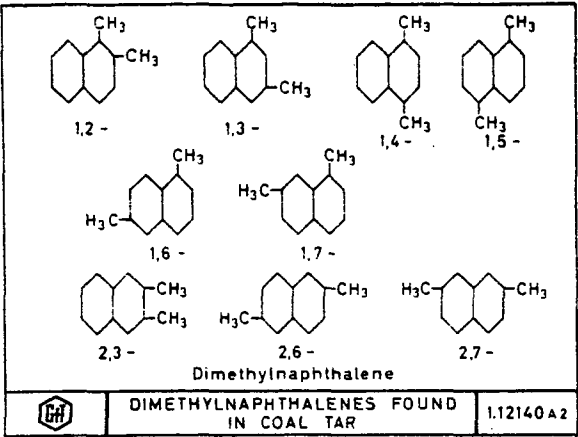


Fig. 34

CATECHOLS FROM THE CARBONIZATION OF NORTH DAKOTA LIGNITE

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INTRODUCTION

Catechol and its methyl homologs occur in a great variety of materials. These include tea, wine, grapes and other fruit, wood products, and coal tar. Of these materials only the last two have been considered as commercial sources for catechol. For example, extensive investigation has been carried out on the destructive distillation of lignin, wood, and bark as possible sources of catechols (1).

Low-temperature carbonization of coal, especially low-rank coals, is a particularly attractive source of catechols if the process can be justified by the improved fuel characteristics of the resulting char, the tar then being treated as a by-product. Also, since catechols are water-soluble, they are found not only in the tar but in the aqueous liquor as well, from which they are easily recovered.

Recovery of catechol from tar and process water has been considered feasible even when relatively low concentrations of the chemical are found. For example, Shono (2) proposes recovery of catechol from aqueous liquor, 50 liters of which contain only 220 grams catechol or 0.5 percent. Williams (3) obtained only 13 grams refined catechol from almost 2 kilograms raw tar (0.6 percent), although he obtained an equal amount of catechol from the associated liquor.

It is the purpose of this paper to show that the low-temperature carbonization products of North Dakota lignite are a rich source of catechol and its homologs.

ANALYTICAL METHODS

Catechols were found in North Dakota lignite tar early in our assay program. In the acid portion of this tar, catechol and the 3- and 4-methyl homologs are exceeded in concentration only by phenol. The relative abundance of these chemicals resulted in their crystallization from distilled fractions of the tar acids and prompted more intensive investigation. Several methods for quantitative estimation of the catechols have been used, depending on the type of mixture involved and the accuracy required.

The most accurate and universally applicable method is column partition chromatography as described by Barker and Hollingworth (4). This consists of a stationary phase of 0.1 N HCl on a support of Celite 535. The mobile phase is cyclohexane to which n-butanol is added in 1-percent increments up to 8 percent. The effluent is examined by UV spectrophotometry in a very sensitive range so that analysis is possible with quite small samples. This method was developed for analysis of ammoniacal liquors, but with slight variations can be used to determine catechols in whole tar.

A more rapid though less accurate method is gas-liquid chromatography of tar fractions or of extracts from the process water. Quantitative results are difficult with complex mixtures, but narrow-boiling fractions of tar acids and extracts of aqueous solutions can be estimated satisfactorily.

A good qualitative method for detecting catechols involves precipitation of their lead salts. The addition of lead acetate to slightly basic aqueous solutions containing catechol or the methyl catechols will result in precipitation of the insoluble lead catecholates. Under favorable conditions the precipitation is sufficiently complete for quantitative results; however, many of the more highly substituted catechols do not form lead salts, especially those substituted in the 3-position, adjacent to an OH (5).

Analysis of Low-Temperature Tar. As previously mentioned, Williams (3) extracted catechol in the amount of 0.6 percent of the raw tar. Gluud and Brauer (5) report the same percentage of catechol in low-temperature tar obtained from a Saar coal. For comparison, low-temperature tar from North Dakota lignite contains 1.0 percent catechol and, in addition, 2.3 percent 4-methyl catechol and 1.5 percent 3-methyl catechol.

Subsequent analysis of tar distillates indicated that the catechols were subject to degradation under conditions of atmospheric distillation. Distilling under vacuum greatly reduced this effect and resulted in considerable enrichment of catechols in the distillate. Tar, vacuum-distilled at 3 mm Hg to the equivalent of 240° at atmospheric pressure, gave an overhead representing 11 percent of the tar: this distillate contained 8 percent catechol, 9 percent 4-methyl catechol, and 0.6 percent 3-methyl catechol. Based on the figures given previously for gross tar, it would appear that there is too much 4-methyl catechol in this distillate and not enough 3-methyl catechol; however, it should be kept in mind that 3-substituted catechols are notoriously unstable and rearrangement or degradation of this material is the rule rather than the exception.

Analysis of Carbonizer Process Water. Catechol and 4-methyl catechol are very soluble in water; 3-methyl catechol, although less soluble than these, can still be classed as soluble. For this reason, virtually every aqueous solution that comes in contact with the tar will extract catechols. This is a recognized fact, as evident from the number of investigations concerning recovery of chemicals from aqueous liquor. Subbarao, et al, (7) extracted carbonizer process water with butyl acetate and found, in addition to catechols, a number of other phenolics. Morgan and Partet (8) extracted up to 1.7 grams catechol per liter of low-temperature carbonization liquid. Similar results have been obtained by others (9, 10, 11).

Butyl acetate extraction was carried out on aqueous liquor from a carbonizer operated at Dickinson, N. Dak. This is a Lurgi-type carbonizer used for production of char briquets from North Dakota lignite (12, 13). Exhaustive extraction of this liquid yielded 37 grams of extract per liter of process water. This extract, analyzed by gas-liquid chromatography, consisted principally of catechol, 3- and 4-methyl catechols with some phenol, cresols, and xylenols also present. Quantitative estimation from the chromatogram indicated 41 percent catechol, 19 percent 4-methyl catechol, and 9 percent 3-methyl catechol in the mixture. Thus a liter of process water contains about 15 grams catechol, 7 grams 4-methyl catechol, and 3 grams 3-methyl catechol. This aqueous liquor is somewhat richer in catechols than those mentioned in the literature, the extraction of which is regarded as commercially feasible.

YIELDS OF CATECHOLS

Carbonization of a ton of lignite at the Dickinson plant yields 5 gallons (42 lb) of tar (70 percent of assay) (12), and 20 gallons of process water (14). Thus from the previous figures we can expect one ton of lignite to yield 0.42 pounds catechol from the tar and 2.5 pounds catechol from the process water for a total of 2.9 pounds catechol per ton of lignite carbonized. Similarly, a ton of lignite should yield 2.2 pounds of 4-methyl catechol and 1.1 pounds of 3-methyl catechol. The amount of catechols actually recovered depends, of course, on the efficiency of the extraction process. While these figures represent the amount of catechols available, it may not be economically feasible to extract the entire amount.

RECOVERY METHODS

The phenosolvan process (7, 15, 16, 20) is the most popular method currently used to extract waste waters. It consists of countercurrent extraction with an ester mixture composed primarily of butyl acetate. Entrained ester is recovered by steam distillation, making the process highly efficient.

This method of recovery can also be used on solutions of buffers used to extract catechols from the tar (3, 17).

Others have extracted aqueous liquors with ether (2, 6), "ketone oil" (9), and cresilic acid (8).

Another interesting method of recovery involves adsorption of phenolics from liquor by activated charcoal (18) or coke dust (10). The phenolics were then desorbed by steam. Catechols were also recovered by precipitation of their lead salts before adsorption of the monohydroxy phenols on charcoal (18).

Separation of Recovered Catechols. Although catechol and 3-methyl catechol boil at about the same temperature (240° and 241° C respectively) at atmospheric pressure, they are separable by distillation under reduced pressure. Thus at 20 mm Hg, 3-methyl catechol has a boiling point of 129° C, whereas that of catechol is 134° and that of 4-methyl catechol is 147° (19).

Separation of catechol and 3-methyl catechol can also be achieved under certain conditions by precipitation of lead salts (5). Similarly 3-methyl and 4-methyl catechols can be separated by precipitation of the 4-methyl catechol with ammoniacal calcium chloride (19).

CONCLUSION

It has been shown that the low-temperature carbonization products of North Dakota lignite are a rich source of catechol, 3-methyl catechol, and 4-methyl catechol. Proven methods are available for recovery and separation of these valuable chemicals. Their potential abundance could result in development of many new uses and in expansion of present applications such as medicinals, antioxidants, plastics, glues, ore flotation, photo developers, and herbicides.

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COMPOSITION OF A LOW-TEMPERATURE BITUMINOUS COAL TAR

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INTRODUCTION

A true low-temperature coal tar is generally defined as that tar produced by carbonizing coal at a temperature not exceeding 500°C. The one outstanding chemical characteristic of a true low-temperature coal tar is the small amount of any individual compound, similar in nature to petroleum and shale oil, and quite different from coke-oven tar in which a single compound, such as naphthalene can account for as much as 10 percent of the tar.

Detailed characterization of low-temperature tars has received little attention until the last few years. Representative of the excellent research being conducted in this field is that of McNeil of the Coal Tar Research Association, Landa of Czechoslovakia, Kalechits and Kuznetsov of Russia, Jäger and Kattwinkel of Germany, Kikkawa and associates of Japan, Kahler and co-workers of Battelle Memorial Institute, Vahrman of Northampton College of Applied Technology, Parant of France, and Brown of Australia. It is outside the scope of this report to review the research of these investigators. The purpose of this paper is to summarize the research carried out by the U. S. Bureau of Mines on a particular low-temperature bituminous coal tar.

The main reason for identifying and determining the amounts of individual compounds in a low-temperature coal tar is to obtain a true picture of the chemical nature of the tar so that refining and utilization can then be approached from a logical standpoint. By this it is not implied that refining will necessarily consist of isolating individual compounds on a commercial scale. However, the results from such studies may indicate that the refining of low-temperature tars will require the development and application of a partly different set of chemical processes to suit the special chemical nature of these tars.

TAR ACIDS

Analytical Procedures and Results

The tar used in this work was made from Arkwright (W. Va.) Pittsburgh-seam, high-volatile bituminous coal in a fluidized carbonization pilot plant at 500°C. The raw tar was de-ashed, dehydrated, and topped to 175°C at the plant. The tar was distilled under very mild temperature conditions, 125°C at a pressure of 133 microns, so as to minimize structural alterations of tar components. For this purpose a rotary vacuum stripper was used. Under these

conditions of distillation, the distillate amounted to about 21 weight-percent of the tar. The tar acids were recovered from the distillate by a Claisen alkali extraction using the procedure of Woolfolk and his associates (19).* The extracted phenols represented 3.54 weight-percent of the tar.

Low-Boiling Tar Acids. The phenols recovered from the distillate were fractionated in a Piro-Glover** micro spinning band still. The mixture of tar acids boiling up to 234°C (at atmospheric pressure) was fractionated in a Perkin-Elmer model 154 chromatographic apparatus using a 12-ft column of 1/4-in. copper tubing packed with Johns-Manville C-22 firebrick, 30 to 60 mesh, containing 34.7 weight-percent di-n-octyl phthalate. The column temperature was 160°C and a carrier-gas flow rate of 150 cc helium per minute was used. The results are shown in Figure 1. Thirteen peaks, or shoulders on peaks were obvious, indicating a minimum of thirteen phenols. Retention times of the substances producing the peaks, relative to peak 1, were determined and compared with the relative retention times of individual pure phenols.

A collecting system, based on one recently described (18), was used to advantage in identifying the components in peaks that were incompletely resolved. By using the collecting system, followed by infrared analysis, identities of the phenols producing the various peaks were confirmed in nearly all instances. By the combination of retention times, infrared analysis of fractions containing more than one phenol, and the peak areas, a reasonably good analysis of a total tar acid mixture boiling up to 234°C was obtained.

High-Boiling Tar Acids. To complete the characterization of the tar acids it was necessary to fractionate and analyze the high-boiling phenols. The method chosen for this complex material was countercurrent distribution, supplemented by ultraviolet and infrared spectrophotometry.

A 200-g portion of tar acids from the tar distillate was distilled at 20 mm through a column filled with glass helices. All the material boiling up to 118° head temperature, equivalent to about 232° at 760 mm, was removed as a single fraction, leaving a residue of 50 g high-boiling phenols or 25 weight percent of the original tar acid mixture. A charge of 41.68 g high-boiling tar acids was distilled at 2.9 mm and a reflux ratio of 20 to 1 in a spinning band still. The infrared spectra were obtained on all of these fractions; they were then combined on the basis of qualitative similarity to give 10 samples and subsequently fractionated by countercurrent distribution, except for the lowest boiling ones.

The instrument used was a 60-tube all-glass model, with 200 tubes in the fraction collector and an automatic robot mechanism. The tube capacity for each phase was 40 ml. The instrument was operated to give 100 to 105 transfers or plates. The average sample size was about 185 mg; the upper phase consisted

* Underlined numbers in parentheses refer to items in the list of references at the end of this report.

** Reference to specific brands is made to facilitate understanding and does not imply endorsement of such items by the Bureau of Mines.

of spectro-grade cyclohexane, and the lower phase was a phosphate buffer made from different proportions of 0.5M Na_3PO_4 and 0.5M Na_2HPO_4 to vary the pH from 9.94 to 11.36. A particular value was chosen because of the suspected presence of certain phenols and their known partition coefficients. After the completion of each fractionation, 8 ml of 1 to 1 hydrochloric acid was added to the tube to neutralize the buffer and mixed well to dissolve the phenols in the cyclohexane.

Ultraviolet spectra were obtained on each cyclohexane solution, and plots were prepared of total absorbance at two informative wavelengths versus tube number. A typical curve is shown in the upper half of Figure 2. On the basis of these plots and the qualitative similarity of the ultraviolet spectra, combinations of the cyclohexane solutions were made for infrared analysis.

On the basis of the combined qualitative results of the ultraviolet and infrared spectra, the constituents from each countercurrent distribution fractionation were distinguished and assigned numbers. The distribution curve of each constituent was readily visualized by following the appearance and disappearance of characteristic absorption bands in the spectra of consecutive countercurrent fractions. This was made easier by the fact that the distributions are essentially Gaussian as well as symmetrical. Distribution peaks observed in this manner always coincided with peaks in the plot of total absorbance versus tube number.

The milligrams of each phenol in each tube were determined from the absorptivities at characteristic wavelengths, as obtained from authentic specimens or literature data. Where such absorptivities were not available, an average absorptivity was obtained from phenols with the most similar structure or, for constituents of unknown structure, from phenols with the most similar absorption bands and boiling points. Plots of milligrams versus tube number were prepared (see bottom half of fig. 2).

Nature of Tar Acids

The results of the qualitative and quantitative analytical procedures for the tar acids are summarized in Table 1. The compounds have been arranged in this table according to groups involving the same fundamental ring structures. Approximately 80 individual compounds were identified, mostly with respect to individual isomers, and the amounts were determined, or estimated, in nearly all instances.

Five different fundamental ring structures were observed among the tar acids. These were:

- | | |
|------------------------|------------------------------------|
| 1. Phenol | 4. Naphthol and Tetrahydronaphthol |
| 2. Indanol and Indenol | 5. Fluorenol |
| 3. Phenylphenol | |

In addition, aliphatic carboxylic acids were present in all boiling ranges, and indanones were present as impurities in a few fractions. The latter were apparently capable of functioning as acids in alkaline solutions, probably through

a keto-enol mechanism. Polyhydric phenols were not present in large enough quantities to detect. As these compounds are quite soluble in the warm discharge water, they were probably effectively extracted from the tar at the plant.

The individual tar acids identified consisted of these seven fundamental structures; mostly methyl groups and some ethyl groups were attached. About 3 tar acids had isopropyl groups, and about 10 had n-propyl groups, but no phenols with butyl groups or higher could be found. Cyclohexyl groups and probably also cycloalkenyl groups were present. A small proportion of alkenyl groups, like propenyl, were likewise present. Alkylphenols with a total of more than 6 carbon atoms in alkyl groups were apparently absent. The most prevalent class of phenol among the high-boiling tar acids was the naphthols.

Nine individual tar acids were identified; each comprised more than 3 weight-percent of the total tar acids and together comprised nearly one-half of the total tar acids. All were low-molecular-weight alkylphenols, as follows: o-, m-, and p-cresol, 2,4-, 2,5-, 3,4-, and 3,5-xyleneol, 2,3,5-trimethylphenol, and 4-ethyl-2-methylphenol.

Complete details of the characterization of the tar acids have been published (10, 11, 12, 15, 16, 20).

TAR BASES

Analytical Procedures and Results

About 3 liters of the low-temperature bituminous coal tar distillate were extracted by the method of Fisher and Eisner (6) to remove tar bases. The tar bases were purified by treatment with solid potassium hydroxide to pH 12, extraction with ether, acidification of the ether extract with sulfuric acid, evaporation of the ether by streaming nitrogen at room temperature, regeneration by adding solid potassium hydroxide to pH 12, extraction with benzene and drying the extract by refluxing under nitrogen in a Dean-Stark apparatus. Distillative removal of the benzene yielded about 40 g dry tar bases, representing about 0.31 weight-percent of the total tar.

A 37.50-g portion of the dry tar bases was fractionated in a Piros-Glover micro spinning band still, using a reflux ratio of 15 to 1, a kettle temperature of about 25° to 186°C, and a head pressure of 80 to 3 mm from the beginning to the end of the run, respectively. Infrared spectra of the tar-base distillate fractions were obtained with a model 21 Perkin-Elmer infrared spectrophotometer and ultraviolet spectra with the Beckman DK-2 spectrophotometer.

These spectra were compared with those of individual compounds that conceivably could be present in the various fractions on the basis of boiling point. The compounds found in the distillate fractions are listed in Table 2. The compounds have been arranged according to groups involving the same fundamental ring structures. Approximately 50 individual compounds were identified, and the amounts were determined, or estimated, in nearly all instances.

Eight different fundamental ring structures were observed among the tar bases. These were:

- | | |
|-------------------------|--------------------|
| 1. Pyridine | 5. Benzoquinoline |
| 2. Cyclopentenopyridine | 6. Aniline |
| 3. Phenylpyridine | 7. N-benzylaniline |
| 4. Quinoline | 8. Naphthylamine |

Two ring structures appeared to be present, although no individual compounds could be identified; these were tetrahydroquinoline and phenylaniline. A special effort was made to identify isoquinoline and its alkyl derivatives, but no indication of their presence was found. These structures covered the boiling range from initial boiling point to about 355°C. It would appear to be certain that the polycyclic structures also would be present in the distillation residue or "pitch."

The individual tar bases identified consist of these eight fundamental structures, with mostly methyl and some ethyl groups attached. One compound with an isopropyl group was identified, but no alkyl groups with chain lengths greater than two carbon atoms were observed. Under the conditions of formation of the tar (500°C), alkyl chains of three or four carbons could conceivably cyclize to form fused saturated rings, as exemplified by cyclopentenopyridines and tetrahydroquinolines. The spectra of alkyl derivatives of these compounds were not available but 2,3-cyclopentenopyridine was definitely identified, and tar-base-distillate fractions 10 to 20 appeared to contain appreciable amounts of alkyl-5,6,7,8-tetrahydroquinolines. There was no doubt, from the ultraviolet spectra of these fractions, that they were rich in some kind of pyridine, that is, compounds with a pyridine ring but no other unsaturated ring in the molecule. Yet the boiling range of these fractions was above the boiling points of the known highly alkylated pyridines. On the other hand, the boiling points of the known alkyl-5,6,7,8-tetrahydroquinolines, which have a pyridine ring but no other aromatic ring, covered the boiling range for fractions 10 to 20 quite closely.

Eight individual tar-base compounds were identified; each comprised more than two weight-percent of the total tar bases and together they comprised fully one-fourth of the total tar bases. All were quinolines, as follows: 2- and 4-methylquinoline, 2,4-dimethylquinoline, 2,4,6-, 2,4,7-, 2,4,8- and 2,6,8-trimethylquinoline, and benzo[f]quinoline. From this standpoint one can say that quinolines, especially those alkylated in the 2- and 4-positions, are the compounds that best typify the tar bases from low-temperature bituminous coal tar and not pyridines, as might have been assumed.

Details of the characterization of the tar bases, including infrared spectral-structural correlations of quinolines, have been published (4, 13, 17).

NEUTRAL OIL

Analytical Procedures and Results

The neutral oil, free of tar acids and bases, was fractionally distilled into 66 fractions. The silica gel adsorption method based on displacement chromatographic techniques, which have been applied to petroleum distillates (7)

and shale-oil naphthas (5), was adapted for separating the aromatic hydrocarbons from saturates and unsaturates. Results of the displacement chromatographic separation are given in Table 3.

Aromatic Hydrocarbons. Aromatic hydrocarbons in the distillate fractions boiling up to 275°C were analyzed by gas-liquid chromatography.

Generally, two methods were followed to identify the aromatic hydrocarbons. The first consisted of (a) preliminary identification of the unknown by comparing its retention time with those of known compounds, and (b) final confirmation of the identity by comparing the infrared spectrum of the collected material with that of the authentic specimen. The chromatograms for two different aromatic cuts, shown in Figure 3, illustrate a good separation in (A) and a complete overlapping of some components in (B), which were subsequently identified and their ratios estimated by infrared spectrophotometry. Table 4 shows the results of the identifications, the peak numbers in the table corresponding to the peak numbers in Fig. 3.

The second method of identification involved the correlation curves of relative retention and boiling points, which were applied in those instances where retention times of authentic specimens were not available.

The aromatic hydrocarbons found in the low-temperature bituminous coal tar and their quantities are presented in Table 5.

Analysis of the aromatic hydrocarbons in the distillate fractions boiling from 275° to 344° is in progress. They are being analyzed by countercurrent distribution using a dual solvent system of 90 weight-percent ethyl alcohol in water for the lower phase and isooctane for the upper phase. Two runs were made on distillate fractions covering the range 275°-282°C, 9 runs on distillate fractions covering the range 287°-344°C and 1 run on the distillate residue boiling above 344°C. In each run 120 transfers were made. Both ultraviolet and infrared spectra are presently being obtained on the contents of each of the 120 tubes. Results to date show that the polycyclic aromatics are essentially completely separated from the paraffins and the olefins, and that the aromatics are separated from each other to a considerable extent. Among the compounds identified are phenanthrene, anthracene, dibenzofuran, carbazole, 1-methylcarbazole, α -olefins, β -branched α -olefins, and trans β (or higher) olefins.

Considerably more detail on the identification of the aromatic hydrocarbons has been described in two earlier publications (1, 2).

C₁₀-C₁₆ n-Paraffins, Isoparaffins and α -Olefins. The non-aromatic hydrocarbon concentrates were obtained from the same neutral oil used in the work on aromatic hydrocarbons. The paraffins and olefins were analyzed by gas-liquid chromatography.

Identification of individual n-paraffins and α -olefins in the non-aromatic cuts was based primarily on retention time. Infrared spectra served mostly for simply confirming the general chemical types. With the exception of 2-methyldecane, authentic specimens of the isoparaffins were not available, so that a somewhat different approach had to be used. It was observed that when the

logarithms of the relative retentions of C_{10} through C_{16} n-paraffins and α -olefins were plotted against their respective boiling points, two parallel, slightly curved lines were obtained. It was assumed that the curve for the 2-methylalkanes would likewise be parallel to the curves for the n-paraffins and α -olefins, and would pass through the one known point for 2-methyldecane. Figure 4 shows the curves for these three chemical types at 170° and 220°.

The individual n-paraffins, isoparaffins, and α -olefins found in the neutral oil, and their amounts, are presented in Table 6.

The quantities of total naphthenes and total trans-olefins were estimated to be only 2.5 percent and 0.5 percent, respectively, of the neutral oil. The quantities of total n-paraffins, total isoparaffins and total α -olefins, however, were determined to be 5.20 percent, 1.03 percent and 2.40 percent, respectively, of the neutral oil. Thus, about three-fourths of the saturates and olefins were made up of the 21 individual compounds that were identified.

Details of this work have been published (3).

PITCH RESINS

Analytical Procedures and Results

The resins from the pitch remaining after the low-temperature bituminous coal tar was distilled were characterized by ring analysis, infrared and ultra-violet spectra, and pyrolysis to structural units. Resins from lignite and sub-bituminous tars were also characterized and are included in this section.

Two different resins were isolated from each pitch: (1) a low molecular weight resin that was insoluble in petroleum ether (boiling range 100° to 115°) but soluble in benzene; (2) a medium molecular weight resin that was insoluble in benzene but soluble in quinoline. The physical properties of these resins are given in Table 7.

The n-d-M method (8) was used for ring analysis. The method is not directly applicable to high oxygen content samples such as coal tar resins since the substitution of an oxygen atom for a methylene group results in an increase in the refractive index and, in particular, in the density of a hydrocarbon. A modification of the n-d-M method was devised that made it possible to obtain acceptable ring analyses of high oxygen content samples (14). A method was also developed for determining the arrangement of rings in polynuclear compounds using the ring index (total rings per carbon atom, R/C) and the atomic hydrogen to carbon ratio (H/C) (9). Seven different series of aromatic ring arrangements were presented ranging from entirely linear structures like phenanthrene, picene, etc., (Series I) to highly globular structures like coronene (Series VII). Data on the number and arrangement of rings in the two low-temperature bituminous resins are given in Table 8.

The resins have four or five aromatic rings and two to six oxygen atoms per molecule. In addition, the lower molecular weight resin apparently has a linear arrangement of rings with one or two saturated rings, while the higher

molecular weight resin has a globular arrangement of rings with five to seven saturated rings. Substituents such as methyl groups, are apparently present, in particular on the lower molecular weight resin.

The infrared and ultraviolet spectra of the resins indicate the following general structure for all of the resins, some features being considerably better established than others. The resins are basically aromatic compounds with mostly isolated single aromatic rings and some clusters of two fused aromatic rings. Saturated rings, possibly including ether groups, probably complete the hydrocarbon skeleton. The major substituents are phenolic hydroxyl groups and, in particular, methyl groups. Most aromatic rings have at least two substituents; these are mostly either methyl groups or fused saturated rings or both. Alkyl substitution is greater for the lower molecular weight resins. Carbonyl groups are present; these are conjugated with either aromatic rings or olefinic groups or both. The hydroxyl groups and carbonyl groups are not on adjacent carbon atoms in at least the great majority of instances, and the carbonyl group is probably not present in a quinone unit.

Insofar as comparisons can be made, these observations are in complete agreement with structural features determined by ring analysis and molecular formula.

Structure determination of the resins was also made by combined pyrolysis and gas-liquid chromatography. The pyrolysis apparatus consisted of a small coil made from a 25.5-in. length of 28-gauge nichrome wire suspended in a stainless-steel chamber connected directly to a gas-liquid chromatographic unit by a short length of 1/8-in. stainless-steel tubing. The chamber, the connecting tubing, and a longer preheating section of tubing were all electrically heated to approximately the same temperature, which was a few degrees below the GLC column temperature. Helium carrier gas passed through the preheat section and the pyrolysis chamber into the column.

The GLC column consisted of a 20-ft length of 1/4-in. copper tubing filled with 75 g packing made from 25 percent Apiezon L grease on 30 to 60 mesh fire-brick. A column temperature of 220°C was used so that relatively high-boiling products, such as phenols and naphthalenes, would be readily detected if present. Gas-liquid chromatographic fractions were collected for infrared spectra.

The semi-solid fraction of the benzene soluble, petroleum ether insoluble resins from a West Virginia bituminous coal tar pitch and a Nugget, Wyoming, subbituminous pitch were pyrolyzed under identical conditions. The resins were pyrolyzed at 528°C in a chamber preheated to 175°C using a sealed glass tube technique. The procedure consisted of placing about 25 mg of the finely divided resin in a glass capillary tube that was then evacuated, sealed, and inserted in the coil. With this size sample and a setting of about 22.5 volts, the tube shattered at 8.4 seconds. The volatile pyrolysis products were swept immediately and directly into the GLC column by the stream of helium.

The chromatograms obtained with the subbituminous and bituminous resins are shown in Figures 5 and 6, respectively. The relative retentions of the pyrolysis products producing the peaks are compared with the relative retentions

of pure compounds in Tables 9 and 10. The relative amounts of pyrolysis products from the two different resins are compared in Table 11. Three compounds were found in the pyrolysis products of the bituminous pitch that were not present for the subbituminous resin. These were 2-methylpentane, 2,3,3-trimethylpentane, and 2,2,3,4-tetramethylpentane. On the other hand, the infrared absorption bands characteristic of different types of olefins, which were readily observed for the pyrolysis products of the subbituminous resin, were absent in the spectra of the pyrolysis products of the bituminous resin.

It can be seen from Table 11 that the proportion of branched paraffins to benzene is considerably less for the pyrolysis products of the bituminous resin than for the subbituminous resin. Also, the proportion of dimethylbenzene is less for the bituminous resin than for the subbituminous resin. These results indicate a lower proportion of saturated, fused multi-ring systems with quaternary carbons for the bituminous resin than for the subbituminous resin. The reason for the apparently complete absence of olefins in the pyrolysis products of the bituminous resin is not known.

A resin molecule containing as part of its structure a unit like 5,6,6a,7,8,12b-hexahydro-6,7-dimethylbenzo[c]phenanthrene could conceivably split up (with, of course, transfer of hydrogen from other structural units) to form 2,3,4-trimethylpentane, as shown in Figure 7. Only those methyl groups required for the formation of 2,3,4-trimethylpentane are shown; additional methyl groups would be present, as determined in previous work. One of the benzene rings in this unit could be released as such, or both benzene rings could be incorporated in the formation of the pyrolysis residue or char. The fact that the resins are rich in oxygen (10 to 15 weight-percent) whereas no oxygen-containing organic compounds could be identified in the volatile pyrolysis products would indicate that the oxygen-containing units in the resin (primarily benzene rings with phenolic hydroxyl groups) are involved in char formation. Under these circumstances there would be a greater proportion of aliphatic compounds than aromatic compounds in the volatile products, such as was actually observed.

Although the pyrolysis results might appear unusual or unexpected, nevertheless the general structure of the resins indicated by these results is the same as that indicated by ring analysis (including ring arrangement), infrared spectra, and ultraviolet spectra.

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TABLE 1. - Summary of tar acids identified in a low-temperature bituminous coal tar and their amounts

Distillable tar acids	Weight-percent ¹	Distillable tar acids	Weight-percent ¹
Phenol	2.3	2-Cyclohexylphenol	0.20
o-Cresol	5.6	2-Alkylcycloalkylphenol I	0.02
m-Cresol	7.2	2-Alkylcycloalkylphenol II	0.01
p-Cresol	4.9	Cycloalkenylphenol I (?) ²	0.005
o-Ethylphenol	1.5	Cycloalkenylphenol II (?)	0.04
m-Ethylphenol	2.5	4-Indanol	0.53
p-Ethylphenol	2.5	5-Indanol	0.49
2,3-Xylenol	1.3	1-Methyl-5-indanol (?)	0.36
2,4-Xylenol	9.1	3-Methyl-4-indanol (?)	0.09
2,5-Xylenol	3.7	4-Methyl-1-indanone (?)	0.15
2,6-Xylenol	1.4	6-Methyl-1-indanone (?)	0.01
3,4-Xylenol	3.7	Alkyl indanone	0.03
3,5-Xylenol	5.9	6-Methyl-5-indanol (?)	0.005
2,3,5-Trimethylphenol	3.3	7-Methyl-5-indanol	0.10
2,3,6-Trimethylphenol	0.01	4-Indenol	0.03
2,4,6-Trimethylphenol	1.4	5-Indenol	0.27
3,4,5-Trimethylphenol	0.13	1-, 2-, or 3-Methyl-4-indenol	0.14
3-Ethyl-2-methylphenol	0.01	Methyl indenol	0.08
3-Ethyl-4-methylphenol	0.01	1-, 2-, or 3-Polyalkyl-4-indenol	0.13
3-Ethyl-5-methylphenol	2.1	3,4-Dinuclearphenol	0.06
4-Ethyl-2-methylphenol	4.5	5,6,7,8-Tetrahydro-1-naphthol	0.02
5-Ethyl-2-methylphenol	0.01	5,6,7,8-Tetrahydro-2-naphthol	0.02
2-n-Propylphenol	0.01	2-Phenylphenol	0.08
3-n-Propylphenol	0.01	3-Phenylphenol	0.03
4-n-Propylphenol	0.13	4-Phenylphenol	0.37
4-Isopropylphenol	0.01	1-Naphthol	0.20
2,3,5,6-Tetramethylphenol (?)	0.04	2-Naphthol	1.54
3-Methyl-5-n-propylphenol (?)	0.29	1-Methyl-2-naphthol	0.02
2-Methyl-5-isopropylphenol	0.01	3-Methyl-2-naphthol (?)	0.008
2-Ethyl-6-n-propylphenol (?)	0.26	4-Methyl-1-naphthol	0.04
3-Ethyl-4-n-propylphenol (?)	0.12	4-Methyl-2-naphthol (?)	0.11
4-Ethyl-3-n-propylphenol (?)	0.24	6-Methyl-2-naphthol (?)	0.01
4-Isopropyl-3-n-propylphenol (?)	0.14	7-Methyl-2-naphthol (?)	0.05
2,4-Di-n-propylphenol (?)	0.13	8-Methyl-2-naphthol (?)	0.02
2,4- or 3,4-Dialkylphenol (?)	0.02	2-Ethyl-1-naphthol (?)	0.85
3-Methyl-2-propen-1-ylphenol (?)	0.003	2,5- or 2,7-Dimethyl-1-naphthol (?)	0.008
Alkenylphenol I	0.005	2,6-Dimethyl-1-naphthol (?)	0.008
Alkenylphenol II	0.001	5,7-Dimethyl-1-naphthol (?)	0.05
Alkenylphenol III	0.03	Methyl-2,3-, or 4-fluorene	0.06

1 The distillable tar acids constitute 3.62 weight-percent of the tar.

2 (?) indicates uncertainty as to which isomer is present.

TABLE 2. - Summary of tar bases identified in a low-temperature bituminous coal tar and their amounts

Distillable tar bases	Weight-percent ¹	Distillable tar bases	Weight-percent ¹
Aniline	0.26	N-Benzyl-2-methylaniline	0.19
3-Methylaniline	0.48	N-Benzyl-4-methylaniline	0.29
2-Ethylaniline	0.22	Quinoline	1.86
2,3-Dimethylpyridine	0.01	2-Naphthylamine	0.63
2,4-Dimethylpyridine	0.45	2-Methylquinoline	2.36
2,5-Dimethylaniline	0.22	4-Methylquinoline	3.21
2,6-Dimethylaniline	0.60	6-Methylquinoline	0.44
3,5-Dimethylpyridine	0.04	7-Methylquinoline	1.02
3,5-Dimethylaniline	0.77	8-Methylquinoline	0.33
N,N-Dimethylaniline	0.06	2,4-Dimethylquinoline	5.92
N-Methyl-2-methylaniline	0.16	2,6-Dimethylquinoline	1.95
2,3,5-Trimethylpyridine	0.58	2,7-Dimethylquinoline	1.36
2,4,6-Trimethylpyridine	0.87	2,8-Dimethylquinoline	1.89
3-Ethyl-4-methylpyridine	0.88	3,4-Dimethylquinoline (?) ²	1.33
4-Ethyl-2-methylpyridine	0.11	4,6-Dimethylquinoline (?)	1.32
5-Ethyl-2-methylpyridine	0.48	2,4,6-Trimethylquinoline	3.41
4-Isopropylpyridine	0.09	2,4,7-Trimethylquinoline	2.85
2,3,4,6-Tetramethylpyridine	0.99	2,4,8-Trimethylquinoline	2.81
2,3,5,6-Tetramethylpyridine	0.24	2,6,8-Trimethylquinoline	2.25
2,6-Dimethyl-4-ethylpyridine	0.45	Acridine (2,3-benzoquinoline)	0.13
3,4-Diethylpyridine (?)	0.63	2,4-Dimethylbenzo[g]quinoline (?)	
2,3-Cyclopentenopyridine	0.16	Phenanthridine (3,4-benzoquinoline)	0.48
Alkyl-5,6,7,8-tetrahydroquinolines (?)		Benzo[f]quinoline (5,6-benzoquinoline)	2.13
2-Phenylpyridine	1.03	Benzo[h]quinoline (7,8-benzoquinoline)	1.64
4-Phenylpyridine	1.21	2,4-Dimethylbenzo[f]quinoline (?)	
2-Methyl-6-phenylpyridine (?)	0.72	2,4-Dimethylbenzo[h]quinoline (?)	
Alkylphenylanilines (?)			

¹ The distillable tar bases constitute 0.31 weight-percent of the tar.² (?) indicates uncertainty as to which isomer is present.

TABLE 3.- Displacement chromatographic separation of neutral oil distillate fractions into chemical types

Distillate fraction No.	Weight of charge, g	Column temperature, °C	Saturates + some olefins		Aromatics + some olefins and some O.S. compounds		Material retained on column, g	Weight of aromatics identified by GLC, g
			n _D range	Total weight, g	Number of fractions	n _D range	Total weight, g	Number of fractions
1 + 2 ¹	1.77	70	1.3930-1.3941	0.74	5	1.3941-1.5007	0.70	4
3 ¹	3.15	70	1.4381-1.4832	0.61	3	1.4832-1.5310	2.29	5
4 ¹	3.60	70	1.4252-1.4471	1.20	4	1.4911-1.5397	2.19	5
5 ¹	7.40	70	1.4328-1.4695	2.11	7	1.4912-1.5545	4.32	9
6 ¹	7.70	70	1.4400-1.4683	1.93	5	1.4895-1.5601	5.21	12
7 + 8 ¹	21	70	1.4025-1.4894	9.98	22	1.4915-1.5658	9.03	11
9 ¹	4.29	70	1.4281-1.4705	1.77	8	1.4995-1.5867	1.94	7
10 + 11 ²	14.93	room temp.	1.4383-1.4938	7.04	18	1.4985-1.5640	6.36	13
12 + 13 ³	12.58	room temp.	1.4321-1.4900	5.00	14	1.4990-1.5790	5.87	13
14 ³	11.16	room temp.	1.4285-1.4769	5.17	13	1.4991-1.5864	5.24	13
15 ³	15.15	room temp.	1.4294-1.4839	6.80	17	1.4971-1.5947	7.31	18
16 ³	13.90	room temp.	1.4400-1.4830	4.11	11	1.5027-1.6039	7.81	18
17 ³	12.70	room temp.	1.4442-1.4843	2.96	9	1.5001-1.6047	6.97	15
18 ³	10.61	room temp.	1.4478-1.5059	3.40	8	1.5331-1.6050	6.14	12
19 ³	15.90	room temp.	1.4378-1.4971	6.05	13	1.5083-1.6005	7.13	13
20 ³	12.20	70	1.4317-1.5050	5.12	13	1.5219-1.5951	5.06	11
21 ³	16.36	70	1.4361-1.5079	6.02	14	1.5179-1.5968	9.11	16
22 ³	17.75	70	1.4386-1.5087	5.17	14	1.5218-1.5989	11.22	22
23 ³	17.14	70	1.4462-1.4988	3.89	9	1.5283-1.5916	12.24	20
24 ³	5.45	70	1.4480-1.5044	1.53	6	1.5449-1.5953	3.52	10
25 ³	16.42	85	1.4375-1.4769	2.20	6	1.5115-1.5970	12.73	23
26 ⁴	17.48	85	1.4395-1.4941	2.36	6	1.5228-1.5983	13.50	28
27 ⁴	17.55	85	1.4390-1.5000	2.25	6	1.5195-1.6014	13.59	23
28 ⁴	19.23	90	1.4349-1.4857	2.96	7	1.5100-1.6025	14.58	25
29 ⁴	10.19	90	1.4375-1.4941	2.03	5	1.5251-1.6040	7.00	12
30 ⁴	2.90	95	1.4698	0.40	1	1.5489-1.6015	2.30	6
31 ⁴	7.88	95	1.4572-1.4743	0.93	2	1.5359-1.6027	5.98	11
32 ⁴	5.96	95	1.4509-1.4888	1.42	3	1.5421-1.5998	3.76	7
33 ⁴	7.66	95	1.4537-1.5048	2.01	3	1.5232-1.5978	4.84	8
34 ⁴	8.33	95	1.4591-1.4916	1.13	3	1.5172-1.5960	6.17	11
35 ⁴	6.00	95	1.4587-1.4835	1.40	3	1.5189-1.5903	3.93	6
36 ⁴	5.99	95	1.4555-1.5136	1.64	4	1.5460-1.6009	3.88	8
37 ⁴	8.74	95	1.4565-1.5171	1.66	4	1.5340-1.5982	6.07	12
38 ⁴	8.71	100	1.4570-1.4878	1.46	3	1.5265-1.5938	6.70	14
39 ⁴	8.69	100	1.4551-1.4710	1.26	3	1.5103-1.5951	6.67	13
40 ⁴	8.34	100	1.4457-1.4865	1.88	4	1.5184-1.6000	6.09	13
41 ⁴	8.58	100	1.4391-1.4841	1.88	5	1.5200-1.6008	5.80	14
42 ⁴	8.42	100	1.4392-1.4790	2.22	6	1.5160-1.6052	5.70	14
43 ⁴	8.62	100	1.4390-1.4820	1.98	5	1.5128-1.6065	6.19	17
44 ⁴	8.83	100	1.4473-1.4895	1.50	5	1.5126-1.6112	6.83	20
45 ⁴	3.14	100	1.4495-1.4669	0.49	2	1.5173-1.5851	2.19	8

1 Desorbent: isopropyl alcohol.

2 Desorbent: butyl alcohol.

3 Desorbent: isobutyl alcohol.

4 Desorbent: cyclohexanol.

TABLE 4. - Identification of components producing elution peaks in the
GLC of two aromatic cuts from distillate fractions 10 + 11
and 26

Peak No.	Relative retention at 220°	Compound identified by I. R.	Relative retention of authentic specimen at 220°
1	1.98	Not identified	--
2	2.08	2-Methylnaphthalene	2.10
3	2.29	1-Methylnaphthalene	2.28
4	2.47	Diphenyl ether	2.47
5	2.56	Biphenyl	2.60
6	2.91	2-Ethylnaphthalene	2.93
7	3.18	{ 2,7-Dimethylnaphthalene	3.13
		{ 2,8-Dimethylnaphthalene	3.17
8	3.30	1,7-Dimethylnaphthalene	3.29
9	3.46	{ 1,3-Dimethylnaphthalene	3.43
		{ 1,6-Dimethylnaphthalene	3.43

TABLE 5. - Analysis of individual aromatic hydrocarbons boiling up to 280° in neutral oil distillate fractions

Compounds identified	Method of identification	Total wt, g	Wt pct in neutral oil ¹
Methylbenzene	Rel. retention	1	Trace
Ethylbenzene	Rel. retention	2	Trace
1,3- and 1,4-Dimethylbenzene	Rel. retention	9	Trace
1,2-Dimethylbenzene	Rel. retention	20	Trace
Isopropylbenzene	Rel. retention	79	Trace
n-Propylbenzene	Rel. retention, I. R.	250	0.002
1-Methyl-3-ethylbenzene	Rel. retention, I. R.	0.010	0.001
1-Methyl-4-ethylbenzene	Rel. retention, I. R.	0.0098	0.001
1-Methyl-2-ethylbenzene	Rel. retention, I. R.	0.0075	0.001
1,2,3-Trimethylbenzene	Rel. retention, I. R.	0.3105	0.045
1,2,4-Trimethylbenzene	Rel. retention, I. R.	0.2695	0.039
1,3,5-Trimethylbenzene	Rel. retention, I. R.	0.1184	0.017
1-Methyl-4-isopropylbenzene	Rel. retention, I. R.	0.0596	0.009
1-Methyl-3-isopropylbenzene	Rel. retention, I. R.	0.0511	0.007
1-Methyl-2-isopropylbenzene	Rel. retention, I. R.	0.0164	0.002
1,2-Diethylbenzene	Rel. retention, I. R.	0.0857	0.012
1,3-Diethylbenzene	Rel. retention, I. R.	0.1009	0.015
1,4-Diethylbenzene	Rel. retention	0.0062	0.001
1,2-Dimethyl-4-ethylbenzene	Rel. retention-bp correlation, I. R.	1.8139	0.260
1,4-Dimethyl-2-ethylbenzene	Rel. retention-bp correlation, I. R.	0.7698	0.110
1,3-Dimethyl-5-ethylbenzene	Rel. retention, I. R.	1.0872	0.156
1,2-Dimethyl-3-ethylbenzene	Rel. retention-bp correlation, I. R.	0.5938	0.085
1-Methyl-3-n-propylbenzene	Rel. retention, I. R.	0.3180	0.046
1-Methyl-2-n-propylbenzene	Rel. retention, I. R.	0.0753	0.011
1,2,4,5-Tetramethylbenzene	Rel. retention, I. R.	1.1066	0.159
1,2,3,5-Tetramethylbenzene	Rel. retention, I. R.	1.7690	0.253
1,2,3,4-Tetramethylbenzene	Rel. retention-bp correlation, I. R.	1.0681	0.153
Indene	Rel. retention, I. R.	0.2331	0.033
3-Methylindene	I. R.	0.7141	0.102
Indan	Rel. retention, I. R.	0.3945	0.057
1-Methylindan	Rel. retention-bp correlation, I. R.	1.1265	0.161
5-Methylindan	Rel. retention-bp correlation, I. R.	1.7566	0.251
4-Methylindan	Rel. retention-bp correlation, I. R.	1.7389	0.249
1,3-Dimethyl-2-n-propylbenzene	Rel. retention-bp correlation	0.0173	0.003
1,2-Dimethyl-3-n-propylbenzene	Rel. retention-bp correlation, I. R.-structural correlation	0.2976	0.042
1,4-Dimethyl-2-n-propylbenzene	Rel. retention-bp correlation, I. R.-structural correlation	0.5974	0.084
1,4-Dimethyl-2-isopropylbenzene	Rel. retention-bp correlation	0.1151	0.017
1-Methyl-3,5-diethylbenzene	Rel. retention, I. R.	0.2393	0.034
1-Methyl-2,4-diethylbenzene	Rel. retention-bp correlation, I. R.-structural correlation	0.9873	0.141
Styrene	I. R.	0.0332	0.005
4-Methylstyrene	I. R.	0.0225	0.003
β-Methylstyrene (trans)	Rel. retention, I. R.	0.1396	0.020
3-Phenyl-1-butene	I. R.	0.1163	0.017
1,2,3,4-Tetrahydronaphthalene	Rel. retention, I. R.	0.6170	0.088
Naphthalene	I. R.	6.3853	0.914

See footnote at end of table.

TABLE 5. - Analysis of individual aromatic hydrocarbons boiling up to 280° in neutral oil distillate fractions - Continued

Compounds identified	Method of identification	Total wt, g	Wt pct in neutral oil ¹
Benzofuran	Rel. retention, I. R.	0.0991	0.014
5-Methylbenzofuran }	I. R.	0.1432	0.021
6-Methylbenzofuran }			
2-Methylbenzofuran }			
3-Methylbenzofuran }	I. R.	0.1681	0.024
7-Methylbenzofuran }			
1,6-Dimethylindan		0.0785	0.011
4,7-Dimethylindan	Rel. retention-bp correlation, I. R.	2.3746	0.340
3-Ethylindene	Rel. retention-bp correlation, I. R.	1.3034	0.186
2-Ethylindene	Rel. retention, I. R.	1.3126	0.188
2,3-Dimethylindene	Rel. retention, I. R.	1.3032	0.186
2-Methyl-1,2,3,4-tetrahydro-naphthalene	Rel. retention, I. R.	1.7762	0.254
6-Methyl-1,2,3,4-tetrahydro-naphthalene	I. R.	1.0426	0.149
1-Methylnaphthalene	I. R.	0.4958	0.071
2-Methylnaphthalene	Rel. retention, I. R.	12.0615	1.728
1-Ethyl-naphthalene	Rel. retention, I. R.	16.1630	2.315
2-Ethyl-naphthalene	Rel. retention, I. R.	1.9777	0.283
2,7-Dimethylnaphthalene	Rel. retention, I. R.	3.1184	0.456
1,7-Dimethylnaphthalene	Rel. retention, I. R.	4.8187	0.690
2,6-Dimethylnaphthalene	Rel. retention, I. R.	4.7915	0.686
1,6-Dimethylnaphthalene	Rel. retention, I. R.	4.1664	0.596
1,3-Dimethylnaphthalene	Rel. retention, I. R.	6.4648	0.926
2,3-Dimethylnaphthalene	Rel. retention, I. R.	6.5617	0.940
1,5-Dimethylnaphthalene	Rel. retention, I. R.	3.8247	0.547
1,2-Dimethylnaphthalene	Rel. retention, I. R.	3.6861	0.528
1,4-Dimethylnaphthalene	Rel. retention, I. R.	3.5632	0.510
2-Methyl-6-ethylnaphthalene }	Rel. retention-bp correlation, I. R.	0.0979	0.014
2-Methyl-7-ethylnaphthalene }	Rel. retention-bp correlation, U. V. and I. R. - structural correlations	3.9029	0.559
1-Methyl-7-ethylnaphthalene and/or	Rel. retention-bp correlation, U. V. and I. R. - structural correlations	3.2925	0.471
1-Methyl-6-ethylnaphthalene }	Rel. retention-bp correlation, U. V.	0.7338	0.105
1,3,6-Trimethylnaphthalene			
1,3,7-Trimethylnaphthalene			
1,2,6-Trimethylnaphthalene }	Rel. retention, I. R.	0.452	0.064
1,2,7-Trimethylnaphthalene }			
Biphenyl	Rel. retention-bp correlation, U. V.	0.8751	--
4-Methylbiphenyl	Rel. retention, I. R.	18.8235	2.696
3-Methylbiphenyl	Rel. retention, I. R.	0.7271	0.104
Cyclohexyl benzene	Rel. retention, I. R.	1.2431	0.178
2a,3,4,5-Tetrahydroacenaphthene	Rel. retention, I. R.	0.2769	0.039
Acenaphthylene	Rel. retention, I. R.	1.1713	0.167
Acenaphthene	Rel. retention, I. R.	0.6963	0.099
Diphenyl ether	Rel. retention, I. R.	2.336	--
2,3-Dimethylbenzofuran	Rel. retention, I. R.	38.5897	5.528
Dimethylbenzofuran II	I. R. - structural correlation	0.1778	0.025
Dimethylbenzofuran III	I. R. - structural correlation	1.7848	0.255
Dibenzofuran	I. R. - structural correlation	0.6451	0.092
	Rel. retention, I. R.	1.4718	--

¹ Total neutral oil distilling up to about 360°, representing 16.92 weight-percent of the total tar.

TABLE 6. - Analysis of individual C_{10} - C_{16} n-paraffins, isoparaffins and α -olefins in neutral oil distillate fractions

Compounds identified	Method of identification	Total wt, g	Wt pct in neutral oil ¹
n-Decane	Rel. retention, I. R.	0.2481	0.036
n-Undecane	Rel. retention, I. R.	1.4842	0.213
n-Dodecane	Rel. retention, I. R.	6.6226	0.949
n-Tridecane	Rel. retention, I. R.	11.2807	1.62
n-Tetradecane	Rel. retention, I. R.	5.5026	0.788
n-Pentadecane	Rel. retention, I. R.	7.3638	1.06
n-Hexadecane	Rel. retention, I. R.	3.7244	0.534
	Total		5.200
2-Methyl nonane	Bp and I. R. -structural correlation	0.1551	0.022
2-Methyl decane	Rel. retention, I. R.	0.2356	0.034
2-Methyl undecane	Bp and I. R. -structural correlation	0.8742	0.125
2-Methyl dodecane	Bp and I. R. -structural correlation	1.4344	0.206
2-Methyl tridecane	Bp and I. R. -structural correlation	1.4000	0.201
2-Methyl tetradecane	Bp and I. R. -structural correlation	2.9188	0.418
2-Methyl pentadecane	Bp and I. R. -structural correlation	0.1367	0.020
	Total		1.026
1-Decene	Rel. retention, I. R.	0.1595	0.023
1-Undecene	Rel. retention, I. R.	1.1871	0.170
1-Dodecene	Rel. retention, I. R.	1.4485	0.208
1-Tridecene	Rel. retention, I. R.	4.5744	0.655
1-Tetradecene	Rel. retention, I. R.	4.3582	0.624
1-Pentadecene	Rel. retention, I. R.	2.8693	0.411
1-Hexadecene	Rel. retention, I. R.	2.1243	0.304
	Total		2.395

¹ Total neutral oil distilling up to about 360°, representing 16.92 weight-percent of the total tar.

TABLE 7. - Physical properties and other data for resins from low-temperature coal tars

Resin No.	Source	Extraction scheme		Yield, weight percent ¹	Molecular weight, M
		Soluble in:	Insoluble in:		
1 A	Bituminous pitch	quinoline	benzene	4.3	628
1 B		benzene	pet. ether ²	64.8	383
2 A	Lignite tar	quinoline	benzene	1.7	510
2 B		benzene	pet. ether ²	22.5	391
3 A	Subbituminous pitch	quinoline	benzene	18.3	603
3 B		benzene	pet. ether ²	40.1	482
4 B	Subbituminous pitch	benzene ³	pet. ether ²	35.8	476 ⁴
4 B'					410 ⁵

Resin No.	Density, d_4^{20}		Refractive index, n_D^{20}	Weight percent		
	As a "solid"	From pyridine solutions		C	H	O ⁷
1 A	1.326	1.326	1.694	76.3	5.3	15.3
1 B	1.129	1.130	1.642	84.3	7.5	6.3
2 A	1.255	--	1.669	81.9	4.3	9.5
2 B	1.155	1.154	1.641	79.4	7.2	11.9
3 A	1.261	1.259	1.669	76.0	5.9	13.5
3 B	1.201	1.200	1.653	78.5	6.7	14.3
4 B	1.159	1.156	1.653	78.8	7.4	10.6
4 B'	1.140	1.141	1.639	81.1	7.8	10.2

¹ On the basis of the specified source.² Petroleum ether, boiling range 100° to 115°C.³ Ratio of solvent to pitch for these two resins: benzene 4 to 1, petroleum ether 20 to 1; ratios for all other resins 25 to 1.⁴ Powdery fraction.⁵ Semi-solid fraction.⁶ From pyridine solutions.⁷ By direct oxygen determination.

TABLE 8. - Number and arrangement of rings in low-temperature tar resins

Resin No.	Ring analysis			Approximate average molecular formula ¹	Corrected ²		Ring arrangement	
	R _T	R _A	R _N		R/C	H/C	Series	Representative hydrocarbon ³
1 A	12.6	5.5	7.1	C ₄₀ H ₃₃ O ₆	0.27	0.99	VII	Octadecahydrodiphenanthrocoronene
1 B	5.4	3.8	1.6	C ₂₇ H ₂₉ O ₂	0.19	1.11	I	Hexahydroheptamethylpicene
2 A	10.1	4.1	6.0	C ₃₅ H ₂₂ O ₃	0.27	0.74	VII	Octahydromethylbenzonaphthocoronene
2 B	4.6	3.8	0.8	C ₂₈ H ₂₈ O ₂	0.16	1.18	I	Tetrahydroheptamethylpicene
3 A	10.3	5.1	5.2	C ₃₈ H ₃₆ O ₅	0.24	1.06	VII	Hexadecahydrohexamethylbenzonaphthocoronene
3 B	6.2	4.5	1.7	C ₃₂ H ₃₂ O ₄	0.17	1.14	I	Tetrahydrodecamethylbenzopicene
4 B	5.8	5.0	0.8	C ₃₁ H ₃₅ O ₃	0.17	1.21	I	Octahydrooctamethylbenzopicene
4 B'	4.9	4.0	0.9	C ₂₈ H ₃₂ O ₃	0.16	1.23	I	Tetrahydrononamethylpicene

¹ Smaller amounts of nitrogen and sulfur not included.² Corrected for oxygen only.³ Picene is given as an example of a linear ring arrangement in Series I; coronene is given as an example of a globular ring arrangement in Series VII; all oxygen atoms, including phenolic oxygen and heterocyclic oxygen, in the resin are rendered as CH₂ groups in these representative hydrocarbons.

TABLE 9. - Relative retentions and infrared absorption bands of pyrolysis products from a subbituminous coal tar resin

Compound	Relative retention ¹		GLC peak No.	Some observed I.R. bands, wavelength, μ	Weight-percent ²
	Pure	Pyrolysis product			
Methane	0.37	0.37	1		
		0.43	2		
		0.49	3		
		0.57	4		
1-Pentene ³	0.60	0.59	5		9.7
2-Methyl-1-pentene ³	0.70	0.71	6		2.7
2,2,4-Trimethylpentane	0.93	0.93	7	7.33, 7.90, 8.03, 8.32, 8.57, 10.21	24.7
Benzene	1.00	1.00	8	2.44, 3.20, 3.25, 5.12, 5.52, 9.65, 14.85	19.3
2,3,4-Trimethylpentane	1.15	1.15	9	7.25, 7.32, 8.93, 9.30, 10.07, 10.32, 10.92	26.9
2,2,4,4-Tetramethylpentane	1.23	1.23	10	8.03, 8.54, 10.28	7.0
Toluene	1.37	1.37	11	9.28, 9.71, 13.74, 14.43	3.5
2,6-Dimethyl-1,4-heptadiene ³	1.53 ⁴	1.55	12		0.5
p-Xylene	1.92	1.93	13	8.95, 12.60 (para)	0.9
m-Xylene				8.57, 9.13, 13.02, 14.53 (meta)	2.1
o-Xylene	2.14	2.15	14	7.22, 8.96, 9.53, 9.81, 13.46	2.7
					100.0

¹ Relative to benzene on Apiezon L grease at 220°C.

² On the basis of the total liquid pyrolysis products.

³ This compound is typical of several equally likely possibilities.

⁴ Retention obtained from log retention-boiling point correlations.

TABLE 10.-Relative retentions and infrared absorption bands of
pyrolysis products from a bituminous coal tar resin

Compound	Relative retention ¹		GLC peak No.	Some observed I.R. bands, wavelength, μ		Weight- percent
	Pure	Pyrolysis product		Pure	Resin	
Methane	0.37	0.37	1			
		0.57	2			
		0.59	3			
		0.62	4			
2-Methylpentane	0.70	0.73	5	8.53, 8.70, 13.51	8.55, 8.72, 13.56	4.1
2,2,4-Trimethylpentane	0.94	0.95	6	7.33, 7.81, 8.03, 8.32, 8.58, 10.22	7.33, 7.81, 8.03, 8.32, 8.58, 10.23	16.0
Benzene	1.00	1.00	7	2.44, 5.12, 5.52, 9.68, 14.85	2.44, 5.12, 5.52, 9.68, 14.88	32.9
2,3,4-Trimethylpentane	1.15	1.17	8	7.23, 7.30, 8.93, 9.31, 10.05, 10.29, 10.92	7.25, 7.33, 8.94, 9.32, 10.06, 10.32, 10.93	26.6
2,3,3-Trimethylpentane ²	1.19			9.20, 9.95, 12.88 ³	9.22, 9.97, 12.93	3.0
2,2,4,4-Tetramethylpentane	1.25	1.26	9	8.05, 8.55, 10.28, 10.93	8.05, 8.55, 10.30, 10.94	7.0
Toluene	1.37	1.39	10	9.26, 9.70, 13.74, 14.43	9.28, 9.72, 13.79, 14.48	5.9
2,2,3,4-Tetramethylpentane ²	1.54	1.57	11	8.33, 8.98, 9.22 ³	8.34, 9.00, 9.24	2.3
p-Xylene				8.93, 12.57	8.95, 12.61 (para)	1.2
m-Xylene	1.92	1.94	12	8.54, 9.13, 13.01, 14.50	8.55, 9.14, 13.04, 14.54 (meta)	0.4
o-Xylene	2.14	2.17	13	8.95, 9.78, 13.47	8.96, 9.80, 13.50 (ortho)	0.6
						100.0

¹ Relative to benzene on Apiezon L grease at 220°C.

² Retention obtained from log retention-boiling point correlations.

³ Bands obtained from A. P. I. Project 44 spectra.

TABLE 11. - Comparison of relative amounts of pyrolysis products from bituminous and subbituminous coal tar resins

Compound	Weights relative to 2,3,4-trimethylpentane	
	Bituminous	Subbituminous
1-Pentene	0.15	0.36
2-Methylpentane	0.60	0.10
2-Methyl-1-pentene	1.23	0.92
2,2,4-Trimethylpentane	1.00	1.00
Benzene	0.11	0.26
2,3,4-Trimethylpentane	0.26	0.13
2,3,3-Trimethylpentane	0.22	0.09
2,2,4,4-Tetramethylpentane	0.09	0.02
Toluene	0.04	0.03
2,2,3,4-Tetramethylpentane	0.01	0.08
2,6-Dimethyl-1,4-heptadiene	0.02	0.10
p-Xylene		
m-Xylene		
o-Xylene		

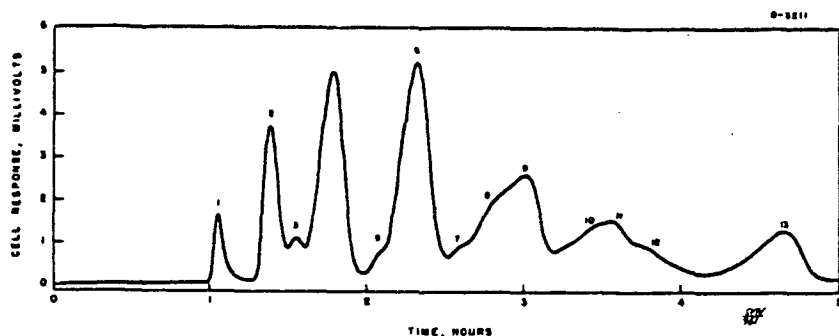


Figure 1. - Chromatogram of Tar Acids From Tar Distillate.

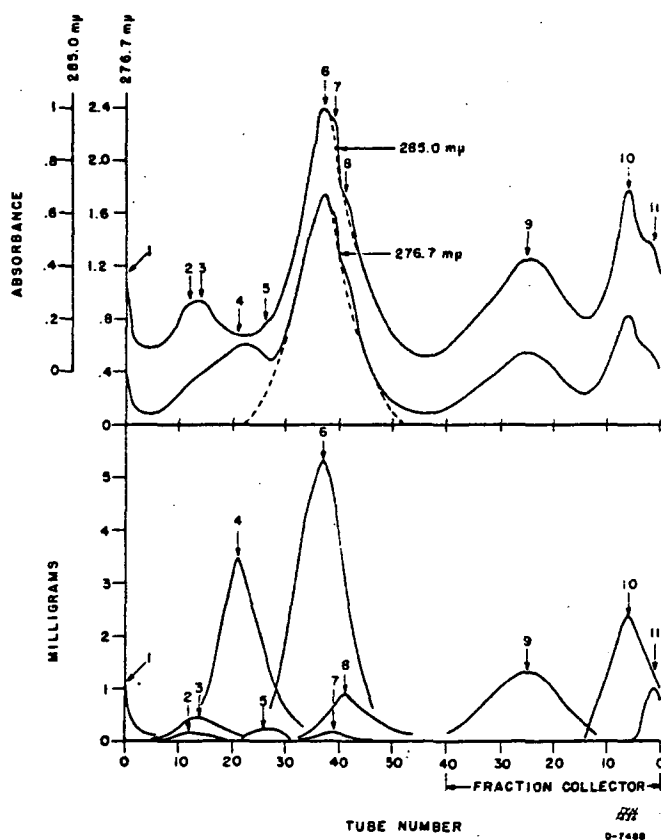


Figure 2. - Countercurrent Distribution of Tar Acids
Boiling 238°-251°C; 100 Transfers;
pH 11.58.

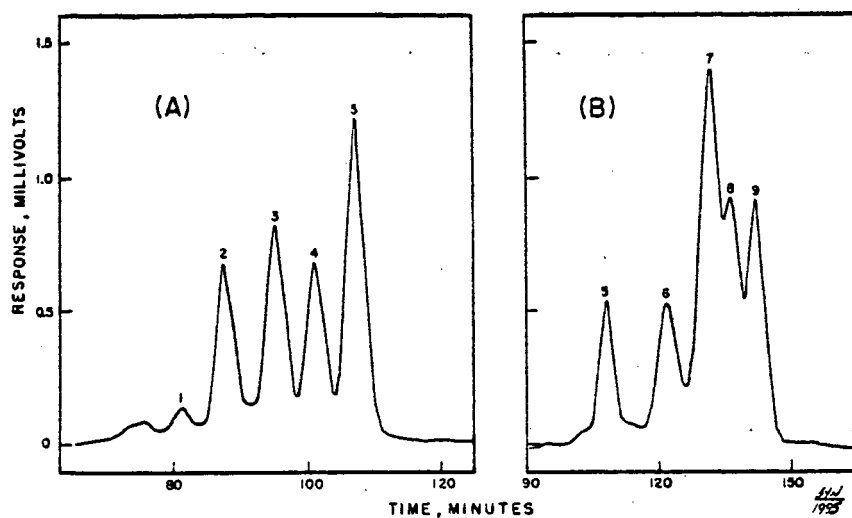


Figure 3. - Chromatograms of Two Aromatic Cuts Obtained From Distillate Fractions 10 + 11 (A) and 26 (B).

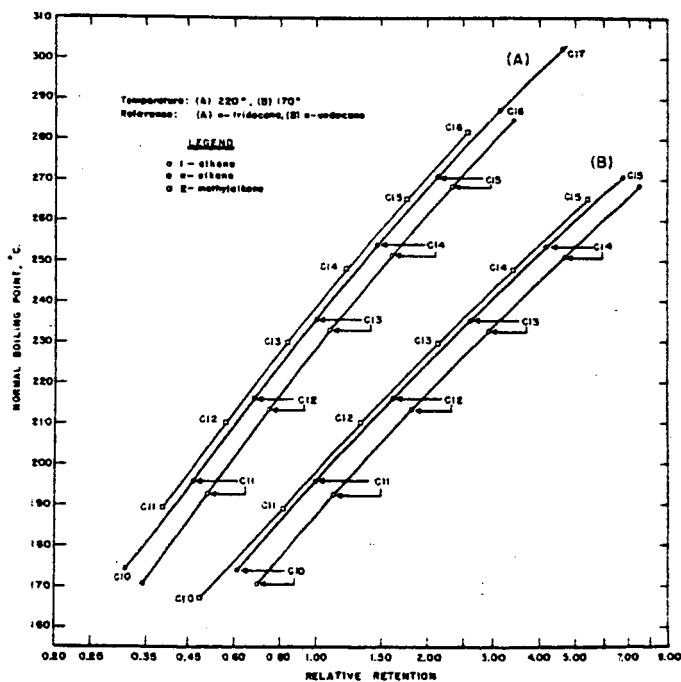


Figure 4. - Correlations Between Boiling Points and Relative Retentions of C_{10} - C_{16} n-Paraffins, Isoparaffins and α -Olefins on Polyphenyl Ether.

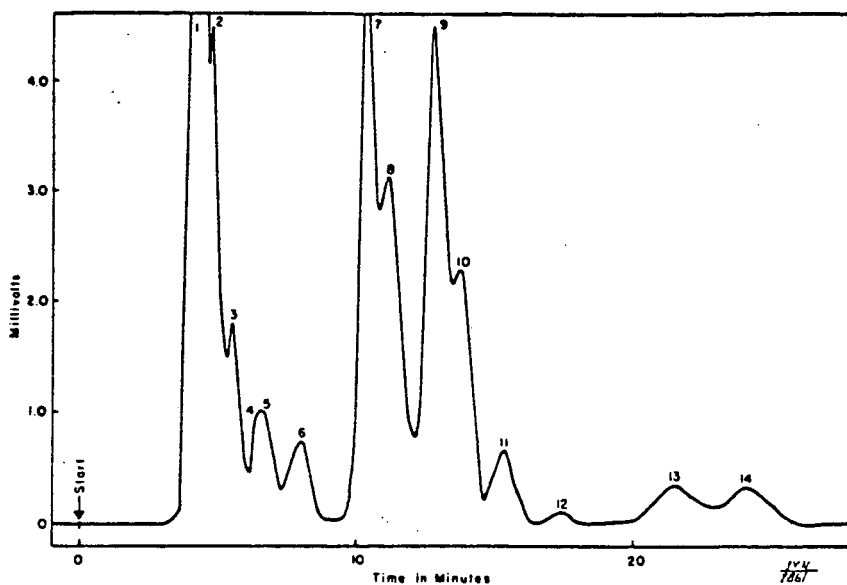


Figure 5. - Chromatogram of Pyrolysis Products From a Subbituminous Coal Tar Resin.

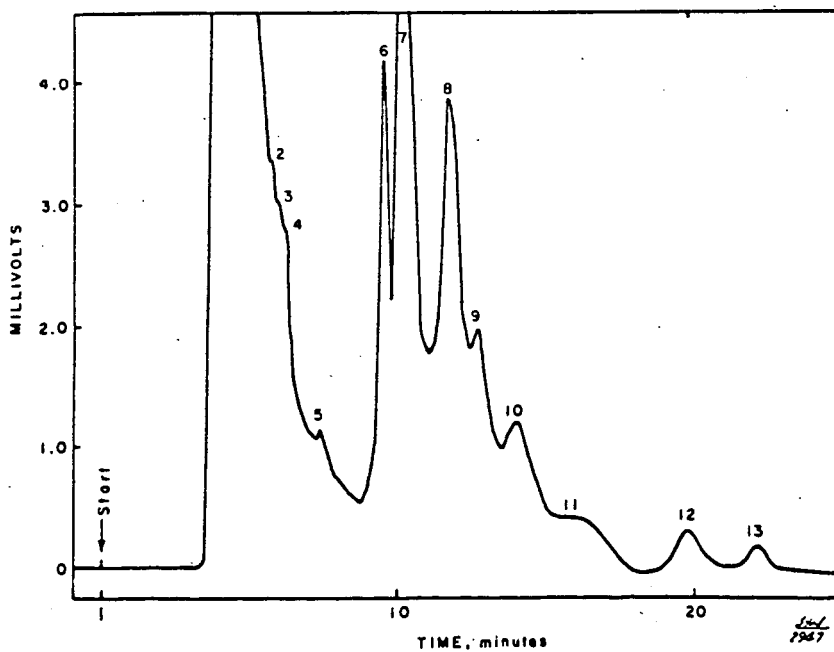


Figure 6. - Chromatogram of Pyrolysis Products From a Bituminous Coal Tar Resin.

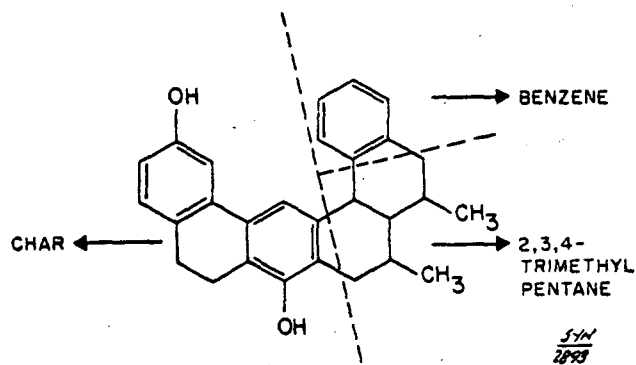


Figure 7. - A Representation of the Pyrolysis of a Hypothetical Resin Molecule.

PRESENT AND FUTURE SUPPLY OF COAL CHEMICALS FROM PETROLEUM SOURCES

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In a discussion of the chemistry and the supply of coal chemicals from petroleum sources, it is essential to define the terminology. In this discussion, coal chemicals will include:

- I The light oil fraction boiling up to 200°C and including primarily benzene, toluene and the mixed xylenes.
- II The middle oil fraction, boiling point (BP) 200-250°C, one of the major components of the total liquid fraction, consisting of tar acids such as phenol, cresols, xyenols as well as higher tar acids. This fraction also contains tar bases such as quinoline. The major component of the middle oil fraction is naphthalene and methylnaphthalene.
- III The heavy oil fraction, BP 250-300°C, containing dimethylnaphthalenes and acenaphthene.
- IV The anthracene oil, BP 300-350°C, containing fluorene, phenanthrene, anthracene and carbazole.

A. Light Oil - Supply Aspects

1. Benzene

Until 1950, benzene produced from coke-ovens and by tar distillers was sufficient for chemical requirements, with imports helping to supply peak demands. When military requirements increased rapidly during the Korean "emergency" and by-product coke-oven capacity was inadequate, petroleum refiners stepped in to take up the slack. The first benzene produced from petroleum appeared in 1950, and in 1961 petroleum benzene accounted for better than 75% of the total production. Table 1 presents historical data on the production and sales of benzene.

The end-use pattern of benzene given in Table 2 is quite extensive, with the main markets being in styrene, phenol, synthetic fibers and synthetic detergents. There will be some market changes, however. Use of benzene to make nylon and detergents has been levelling off at an annual growth rate of 3 to 5%. In the future, the big markets will be styrene and phenol.

In 1961, benzene production and sales were 545 and 431 million gallons, respectively. It is expected that by 1971, production will amount to approximately 840 million gallons, a 4.4% annual increase. The past and estimated future benzene production figures are presented graphically in Figure 1.

Table 1 - BENZENE PRODUCTION AND SALES, 1950-1961

Year	Production				Sales
	Tar Dist.	Coke-Oven	Petroleum	Total	
1950	22.0	162.2	10.1	194.3	172.6
1951	19.0	178.0	32.6	229.5	239.2
1952	19.0	155.1	35.5	209.6	217.0
1953	19.0	178.8	63.0	260.8	232.7
1954	15.0	142.8	91.9	249.7	202.0
1955	15.0	174.2	98.6	287.8	264.8
1956	15.0	174.4	111.6	301.0	284.5
1957	13.0	181.1	116.2	310.2	276.5
1958	9.0	119.8	142.1	270.8	243.3
1959	10.0	120.3	208.8	339.1	330.5
1960	12.8	135.3	309.2	457.3	377.4
1961	12.4	120.2	412.8	545.4	431.0

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Table 2 - BENZENE END-USE PATTERN AS OF 1960

	Percent of Total
Aniline	4.1
Benzene Hexachloride	0.4
DDT	4.1
Maleic Anhydride	2.8
Nylon	7.8
Phenol	23.4
Styrene	47.4
Synthetic Detergents	7.0
Dichlorobenzene	2.3
Other Non-Fuel Uses	0.5
Motor Grade	0.2
	<u>100.0</u>

-0-

2. Toluene

Toluene from petroleum sources has attained a very important status in the past decade. Of the 260 million gallons of toluene produced in 1961, 88% were petroleum derived, with the remainder supplied by coke-ovens and tar distillers. In 1950, petroleum toluene accounted for only 54% of the 84 million gallons produced. Table 3 presents historical production-sales trends for toluene.

The largest end-use for toluene as of 1960, as shown in Table 4, is as a high octane blending agent in motor and aviation gasolines. This outlet, however, is declining rapidly because of the advent of jet aircraft and the emphasis on regular-gasoline economy. These facts, along with a benzene shortage, combined for a time to create a disposal problem for refiners and made the conversion of toluene into benzene by hydrodealkylation an attractive process. This has resulted in an increase in benzene production which has satisfied the present demand. Other uses of

Table 3 - TOLUENE PRODUCTION AND SALES, 1950-1961

Year	Production				Sales
	Tar Dist.	Coke-Oven	Petroleum	Total	
1950	7.7	30.7	45.5	83.9	70.3
1951	11.4	34.3	55.7	101.4	82.4
1952	10.8	30.5	64.0	105.3	87.5
1953	4.7	36.0	115.5	156.2	90.9
1954	2.9	33.4	122.9	159.2	126.2
1955	3.9	38.2	143.4	185.5	138.3
1956	5.6	37.2	130.8	173.6	135.2
1957	4.7	38.0	154.9	197.6	130.0
1958	4.2	28.0	207.4	239.6	136.6
1959	3.7	26.9	251.0	281.6	166.8
1960	3.2	30.4	240.8	274.4	200.1
1961	3.1	28.5	228.3	259.9	162.9

-θ-

Table 4 - TOLUENE END-USE PATTERN AS OF 1960

	Percent of Total
Motor Gasoline	50.5
Aviation Gasoline	18.6
Solvents (chiefly for Nitrocellulose Lacquers)	13.6
TNT	2.3
Detergents (Toluene Sulfonates)	1.8
Toluene Diisocyanate	1.4
Benzene*	0.4
Miscellaneous Chemicals (Benzoic Acid, Benzaldehyde, Benzoyl Chloride, Phenol, etc.)	11.4
	100.0

* In 1961, with the installation of many hydrodealkylation units by various companies, the consumption of toluene for benzene production was expected to increase to 60 million gallons. 1960 consumption was 1 million gallons.

-θ-

toluene shown in Table 4 are in the manufacture of chemicals, such as toluene diisocyanate and toluene sulfonate, and as a solvent for paints and nitrocellulose lacquers.

The present requirements of toluene also appear to be met. However, the development of additional processes, such as Dow's phenol-from-toluene process and DuPont's caprolactam-from-toluene process may play a major role in increasing the demand for more toluene. It is expected that by 1971, toluene production will amount to 450 million gallons, a 5.6% yearly increase. The past and estimated future toluene production figures are also presented in Figure 1.

3. Xylenes

The xylene aromatics are coal-tar chemicals which are also derived from petroleum and are being extracted by refiners and separated for chemical consumption to an increasing extent. Of

the 257 million gallons of mixed xylenes produced in 1961, 96.9% were derived from petroleum, 2.9% from coke-ovens and 0.2% from tar distillers, as will be seen from Table 5.

Table 5 - MIXED XYLENES PRODUCTION AND SALES, 1950-1961.

Year	Production				Sales
	Tar Dist.	Coke-Oven	Petroleum	Total	
1950	1.5	8.0	62.4	71.9	56.4
1951	2.2	9.1	64.4	75.7	58.5
1952	2.1	8.1	61.6	71.8	57.8
1953	0.7	9.9	102.9	113.5	65.6
1954	0.5	10.0	99.7	110.2	66.5
1955	0.6	11.3	96.1	108.0	77.6
1956	1.9	10.3	124.1	136.3	85.3
1957	1.3	10.8	115.1	127.2	83.0
1958	0.6	8.4	191.5	200.5	95.1
1959	0.5	7.5	233.5	241.5	128.8
1960	0.4	8.1	274.0	282.5	141.5
1961	0.5	7.6	249.2	257.3	124.0

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The major outlets for xylenes are in fuels, solvents and chemical uses, shown in Table 6. Gasoline octane improvement is the largest outlet for xylenes, and nothing will change this for a long time. Xylenes face the same problems as toluene, with aviation gasoline demand decreasing and motor gasoline needs being somewhat indefinite at the present time. Solvent uses claim approximately 17% of the mixed xylenes production.

Table 6 - XYLENES END-USE PATTERN AS OF 1960

	Percent of Total
Gasoline	61.0
Solvents	17.5
ortho-Xylene	6.3
meta-Xylene	1.7
para-Xylene	9.6
Miscellaneous Chemicals (Herbicides, Plasticizers, Chlorinated Xylene, etc.)	3.9
	<u>100.0</u>

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For chemical synthesis, the xylenes fraction is separated into the pure isomers -- ortho, meta, and para -- the consumption of which is shown in Table 7 for 1959 - 1961. Ethylbenzene is also obtained during the separation process. Composition of a petroleum derived mixed-xylenes stream is variable but generally contains the three isomers and ethylbenzene in the following proportions:

Ethylbenzene	8.6 - 13.2 %
<u>para</u> -Xylene	17.1 - 20.3 %
<u>meta</u> -Xylene	45.5 - 52.2 %
<u>ortho</u> -Xylene	18.0 - 24.4 %

Table 7 - XYLENE ISOMERS CONSUMPTION 1959 - 1961

Year	Millions of Gallons		
	Consumption		
	<u>ortho-Xylene</u>	<u>meta-Xylene</u>	<u>para-Xylene</u>
1959	8.4	2.1	22.0
1960	16.3	4.4	24.8
1961	22.3	5.5	26.5

-9-

a. Para-Xylene

Para-xylene is currently the most important of the xylene isomers. Recent production of para-xylene is 280 million pounds (39 million gallons) per year. It is used primarily to make terephthalic acid which is usually sold as the dimethyl terephthalate ester for the production of polyesters such as DuPont's Dacron fiber and Mylar film.

b. Ortho-Xylene

Ortho-xylene is the second-most important isomer and could become another major feedstock for phthalic anhydride, now that improved catalyst and plant designs have increased yields to a respectable level. In the past, ortho-xylene was considered a poor substitute for naphthalene because the yield was only half of the theoretical of 1.39 lb/lb of feed, while naphthalene yielded three-fourths of the 1.16 lb/lb theoretical. Present ortho-xylene capacity is 650 million pounds per year. About 80% of the future production from these facilities is destined for export to Europe and Japan where it will be used to make phthalic anhydride.

c. Meta-Xylene

The most plentiful isomer, meta-xylene, which makes up about 50% of the xylene isomer mixture, is the least useful. Meta-xylene is used to make isophthalic acid, which competes with phthalic anhydride for the reinforced plastic and plasticizer market. One refiner separates meta-xylene for isophthalic acid production and another produces isophthalic from mixed xylenes along with terephthalic acid. The chief use for meta-xylene is for solvent and gasoline blending after the more valuable xylenes have been extracted.

The past and estimated future production figures for xylenes are shown graphically in Figure 1.

B. Light Oil - Chemistry and Chemical Engineering Aspects

The chemistry and chemical engineering of the production of light oil aromatics from petroleum are of considerable interest. The problem is that of the conversion of a suitable raw material and the separation of the aromatics from the residual paraffinic and naphthenic hydrocarbons. Although the chemistry of the production of benzene from petroleum sources is very similar to that of the production of toluene and xylenes, some subtle differences do exist in both chemical and the chemical engineering aspects of the problem.

In the case of benzene, a suitable raw material is one which contains substantial proportions of cyclohexane and methylcyclopentane. Table 8 shows the composition of the fraction which contains the two benzene precursors in various straight-run gasolines.⁽¹⁾ It will be observed that the total naphthenes will vary from approximately 20 to about 55 percent of the total fraction and

this fraction in return ranges from about 10 to 18 percent of the total C₅ to 360°F gasoline. This table indicates that the potential benzene production from straight-run gasoline is extremely high, to say nothing of the substantial amounts of methylcyclopentane and cyclohexane being currently produced synthetically by the hydrocracking processes which are now coming into commercial operation.

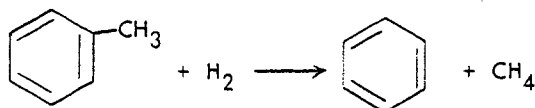
Table 8 -

COMPOSITION OF 140-185°F FRACTIONS FROM
VARIOUS STRAIGHT-RUN GASOLINES

Hydrocarbon, Vol.-%	Source						
	Ponca City Okla.	East Texas	Bradford Pa.	Greendale Mich.	Winkler Texas	Midway Calif.	Conroe Texas
2-Methylpentane	9	15	22	7	17	14	11
3-Methylpentane	8	12	13	5	42	10	8
n-Hexane	41	31	37	63	11	16	17
2,2 & 2,4-Dimethylpentane	2	6	6	2	8	4	3
Methylcyclopentane	20	23	9	9	15	34	21
Cyclohexane	16	12	12	11	6	21	31
Benzene	4	1	1	3	1	1	9
Total Naphthenes	36	35	21	20	21	55	52
Percent of 140-185°F Fraction Based on C ₅ -360°F Gasoline	13	16	15	18	10	12	14

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As mentioned earlier, some benzene is also produced by the hydrodealkylation of toluene. Various processing schemes have been proposed. The Hydeal* process is a catalytic operation which converts toluene concentrates into benzene in the presence of recycled hydrogen. Since the process consumes hydrogen in the formation of benzene and methane, as shown by the equation:

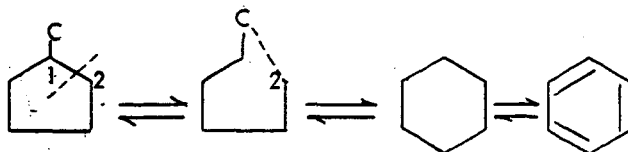


the units are equipped with internal hydrogen enrichment facilities so that the available hydrogen in the make-up gas can be utilized efficiently.

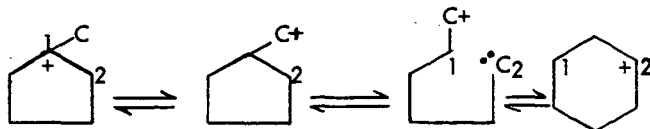
Another possible source of benzene is represented by the normal hexane which is a substantial component of the straight-run fractions. In fact, some of the early work in catalytic reforming has been directed on the dehydrocyclization of normal hexane to benzene and normal heptane to toluene. However, it should be pointed out that under conditions which induce a very high conversion of the naphthenic hydrocarbons to benzene, the conversion of hexane to benzene is very slight. Consequently, the bulk of the benzene is derived at the present time by processing fractions containing methylcyclopentane and cyclohexane.

The chemistry of the conversion of cyclohexane and methylcyclopentane is of considerable interest. Cyclohexane can be converted to benzene in the presence of a platinum-containing catalyst at exceedingly high rates. However, under the same conditions, methylcyclopentane is virtually unreacted. The reason for this lies in the need for rearrangement of the methylcyclopentane molecule to a cyclohexane intermediate prior to the conversion to benzene. This rearrangement reaction requires a bond breakage and the formation of a new bond as shown in the following:

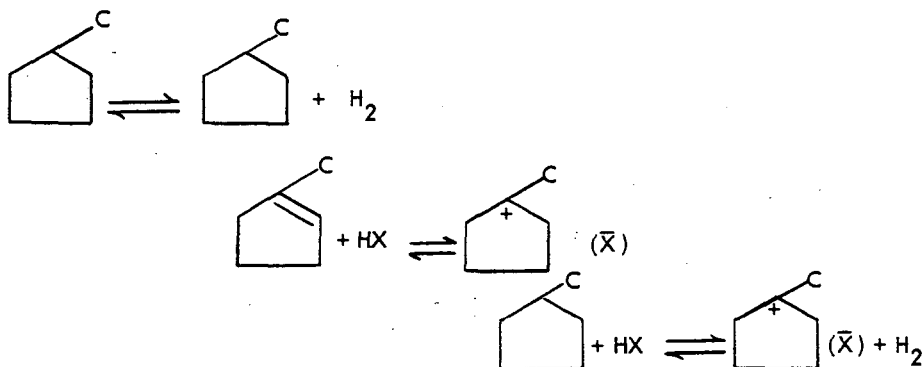
* Trademark



In detail, the carbonium ion mechanism which is involved in such a rearrangement calls for the formation of a tertiary carbonium ion with the subsequent shift to a primary carbonium ion and its addition at the second carbon atom, thus effecting the ring closure:



It will be observed that a cyclohexyl carbonium ion is produced. It is converted to cyclohexane in the reverse manner of the initial formation of the methylcyclopentane carbonium ion:



As pointed out above, in the absence of an acid catalyst no reaction of methylcyclopentane will take place, and a so-called bi-functional catalyst is required. This bi-functional property implies the balanced presence of both dehydrogenation-hydrogenation and acid activities. The proper balance is quite critical; otherwise, methylcyclopentane may be converted directly into hexane instead of cyclohexane.

We have found that a balanced catalyst is obtained by a specially prepared composite of aluminum, platinum and halogen, such as fluorine or chlorine. The conversion of methylcyclopentane is then readily carried out at about 450-500°C and about 20 atmospheres pressure in the presence of recycle hydrogen. The dehydrogenation under pressure in the presence of recycle hydrogen is now well-established in petroleum technology. Under these conditions, a clean catalyst surface is maintained so that long on-stream times are readily achieved.

It should be further pointed out at the conditions of operation the thermodynamic equilibrium among the three species, cyclohexane, methylcyclopentane and benzene, are such that the end product should contain a substantial amount of benzene, a very small amount of cyclohexane and an intermediate amount of methylcyclopentane. Therefore, it is imperative that there be a rapid conversion of the cyclohexane to benzene, so that methylcyclopentane may be converted into cyclohexane and the latter removed from the system in the form of benzene as rapidly as possible.

Unless this is done, methylcyclopentane cannot be converted into cyclohexane and will undergo undesirable side reactions such as the formation of hexanes.

The argument may be raised regarding the existence of the cyclohexane intermediate in the conversion of methylcyclopentane into benzene. In connection with this, we have carried out a study which provides a reasonable answer to the problem. This study involved the poisoning of the catalyst system by means of sulfur and observing the effect of the poison upon the conversion of cyclohexane and methylcyclopentane. The rate of cyclohexane conversion is normally much greater than that of methylcyclopentane. Therefore, if the cyclohexane rate is poisoned, the methylcyclopentane rate should not be affected until the cyclohexane rate is poisoned to the extent that it falls below the normal methylcyclopentane rate. This is essentially what has been found experimentally, as will be observed from Figure 2. Thus the indications are that at least the same intermediate is involved in the conversion of both cyclohexane and methylcyclopentane.

As might be expected, the conversion of C₇ and C₈ naphthenes into toluene and xylenes, respectively, also proceeds very readily over the bi-functional catalyst. It should be pointed out that, as the molecular weight is increased, the rate of the conversion of C₅ ring naphthenes rises rapidly. This is quite understandable on the basis of a considerably increased number of possible carbonium ions. The same is true for paraffinic hydrocarbons, so that higher aromatics are readily obtained from higher paraffins by the dehydrocyclization reaction.

It should be mentioned that under the usual operating conditions, the bi-functional catalyst will effect an equilibration among the isomers of the higher aromatics, so that the product will exhibit a composition closely approximating the thermodynamic equilibrium. However, it is possible to reduce the extent of equilibration by a proper selection of charging stock and operating conditions. Although ethylbenzene is not truly a coal chemical, it is an important intermediate for the production of styrene, and is normally prepared by the alkylation of benzene with ethylene.

With almost half of the benzene market going to styrene manufacture, refiners are taking a closer look at ethylbenzene separation from xylene by super-fractionation to compete with benzene alkylation as a styrene intermediate. Ethylbenzene from this source has a maximum potential of only 70 million gallons (505 million pounds) per year based on present xylene production and cannot replace benzene as a styrene feedstock but could take a share of the market. Economics of ethylbenzene separation depends greatly on the concentration of ethylbenzene in the mixed aromatics, which varies from crude to crude.

In one of our studies on ethylbenzene, we have investigated the possibility of producing ethylbenzene in high concentrations from straight-run fractions. Ethylbenzene is unique in one respect and that is that its direct precursor, ethylcyclohexane, is the highest boiling C₈ naphthene. Thus, by proper selection of the charging stock and operating conditions which do not cause excessive equilibration, it is possible to attain high ethylbenzene concentrations in the product.

The following procedure was employed. A so-called pre-xylene fraction in the Engler boiling range of 123 to 132°C was hydrogenated and subsequently distilled into 20 cuts. Each cut was processed over the bi-functional catalyst and the aromatic product distribution was determined. The following is the summary of the results:

Cut No.	BP, °C	Percent Distribution of the Aromatic Portion			
		p-Xylene	m-Xylene	o-Xylene	Ethylbenzene
1	116.8	24.9	58.3	16.8	0
5	122.0	21.6	55.9	20.3	2.2
10	126.5	13.2	34.7	33.1	19.0
14	131.1	2.5	4.1	13.5	79.9
15	132.6	2.6	0.3	14.0	83.1
16	133.9	1.1	1.9	7.6	89.9
17	134.9	1.6	2.0	8.5	87.9

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It will be observed that very high concentrations of ethylbenzene may be produced directly. Since ortho-xylene is the main impurity at the high concentrations of ethylbenzene, it can be readily separated to produce ethylbenzene fractions having a purity in excess of 95%. The above example serves to demonstrate the high versatility of a method involving variations in charging stock, catalyst and operating conditions.

The presence of a substantial number of hydrocarbons which may be converted into specific aromatic compounds has as one drawback the variable amounts of other charging stock components which remain in the aromatic product. Thus, the extremely rapid rise in the rate of production of lower aromatics would not be possible without the concurrent development of methods of separation of these aromatics from the other hydrocarbon components. These methods involve extraction by liquids and solids. One method which has received wide commercial acceptance is the Udex^(R) process, (2) which employs a glycol-water mixture as a selective solvent. Originated by Dow Chemical Company and developed by Universal Oil Products Company, this process combines a high selectivity with a minimum utility requirement. Aromatics are recovered as a hydrocarbon type with a subsequent fractionation to produce pure benzene, toluene and mixed xylenes. It is interesting that the selectivity of separation is highest for benzene and decreases with increasing molecular weight.

C. Hydrocarbon Components Of Higher Boiling Fractions

Petroleum sources represent a virtually unlimited supply of polynuclear aromatics. The widely used catalytic cracking process produces, along with gasoline and gaseous hydrocarbons, a higher boiling fraction called cycle oil. This fraction is characterized by a high resistance to further catalytic cracking and contains a substantial amount of polynuclear aromatics. These aromatics are formed through a series of reactions involving removal of larger side chains, isomerization and dehydrogenation. The last reaction is in reality a hydrogen transfer reaction, wherein the hydrogen content of the lower boiling fraction is enriched at the expense of the higher boiling fraction. The usual composition pattern of the aromatic portion of cycle oil is extremely complex from the standpoint of the number of isomers; however, the actual composition by broad hydrocarbon class is much simpler in that the bulk of the material is represented by methylated polynuclear compounds. This is due to the fact that the less stable species are eliminated in catalytic cracking to give lower boiling compounds, leaving behind an equilibrated, highly stable structure. Typical components are mono- and dimethylnaphthalene followed by the methylated derivatives of tri- and tetra-ring condensed structures.

The removal of methyl groups followed by proper separation procedures represents a reasonable way of obtaining a variety of polynuclear compounds from petroleum sources. Such methods become particularly attractive when other sources cannot meet the demand. In the case of naphthalene, the coal-tar industry has dominated the market for many years, with an annual production of

500 million pounds. It should be remembered, however, that naphthalene, like ortho-xylene, is closely tied to the phthalic anhydride industry, with three-fourths of all naphthalene going to phthalic anhydride manufacture. Phthalic manufacturers have been hard-pressed at times to meet their phthalic demand because of a naphthalene shortage resulting from low steel production rates. In times of naphthalene shortage, ortho-xylene has been substituted in naphthalene-designed plants. This situation has also created a sizeable petroleum-naphthalene market. Thus, the hydro-dealkylation route is expected to become a major source of supply of this important chemical. Petroleum-naphthalene's high purity has provided an unexpected bonus in higher phthalic yields, making petroleum-naphthalene a much sought after chemical. Dependability of supply is another factor that has helped petroleum-naphthalene sales.

Despite ortho-xylene's invasion of the phthalic anhydride market, naphthalene consumption is expected to increase, reaching a figure of approximately one billion pounds by 1971, as illustrated in Figure 3. The naphthalene production and sales statistics are shown in Table 9.

Table 9 - CRUDE NAPHTHALENE STATISTICS
Millions of Pounds - (74 - 79°C)

Year	Production			Sales
	Coke-Oven	Tar Dist.	Total	
1950	99.7	188.8	288.5	206.7
1951	131.1	224.6	355.7	255.3
1952	106.9	215.6	322.5	209.8
1953	112.9	162.9	275.8	200.1
1954	100.1	195.1	295.2	224.2
1955	184.2	292.9	477.1	338.7
1956	177.3	314.2	491.5	289.0
1957	N.A.	N.A.	420.3	276.0
1958	N.A.	N.A.	345.1	212.6
1959	N.A.	N.A.	425.3	266.5
1960	N.A.	N.A.	517.0	310.3
1961	N.A.	N.A.	497.2	299.1

PRODUCTION AND SALES OF THE THREE GRADES AS OF 1960

	Millions of Pounds	
	Production	Sales
Solidifying at less than 74°C	24.7	26.0
Solidifying at 74°C to less than 76°C	21.5	10.2
Solidifying at 76°C to less than 79°C	470.9	274.1

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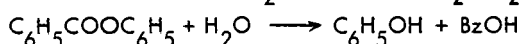
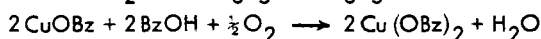
As pointed out above, other coal hydrocarbons can be produced from petroleum when the demand arises. The newly developed methods of separation, ⁽³⁾ based on differences in carbon-to-hydrogen ratios, can be used to provide hydrocarbon classes which can subsequently be demethylated and further purified by conventional means, such as distillation and crystallization.

D. Tar Acids

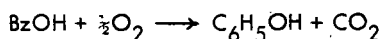
The tar acids are represented by phenol, cresols, cresylic acids and xylenols. The production of phenol from petroleum sources has grown very rapidly and five different processes are currently used:

1. Chlorobenzene Hydrolysis
2. Benzene Sulfonation
3. Cumene Peroxidation
4. Raschig Method
5. Two-Step Oxidation

Of these, the first three supply the bulk of the market. The cumene peroxidation process has been gaining in popularity and most of the new plants will employ this procedure. The two-step oxidation method is of considerable interest in that the starting material is toluene, which is oxidized to benzoic acid followed by the copper catalyzed oxidation to form phenylbenzoate and subsequent hydrolysis to produce phenol and benzoic acid. The reactions are believed to take place in the following manner:⁽⁴⁾



Overall Reaction:



The reaction can also be applied to the production of various cresols starting with toluic acids, as well as 2-naphthol using 1- or 2-naphthoic acids as raw materials. Synthetic phenol capacity in the U. S. is presently about 940 million pounds per year. If all announced plans for expansion and new plants materialize, capacity will be over 1.2 billion pounds by the end of 1963. Table 10 presents historical production and sales data.

Table 10 - PHENOL PRODUCTION AND SALES, 1950-1961

Millions of Pounds								
Production								
Year	Synthetic			Natural			Total	Sales
	Cumene	Other Processes	Total	Coal Tar	Petroleum	Total		
1950	-	291.9	291.9	-	-	20.2	312.1	199.8
1951	-	364.6	364.6	-	-	23.8	388.4	244.0
1952	-	316.2	316.2	-	-	21.6	337.8	187.6
1953	-	356.8	356.8	-	-	25.6	382.4	199.5
1954	19.2	377.5	396.7	-	-	20.8	417.5	218.6
1955	69.7	405.3	475.0	37.9	3.8	41.7	516.7	280.3
1956	93.8	415.6	509.4	34.5	5.3	39.8	549.2	302.6
1957	100.7	413.8	514.5	33.8	8.0	41.8	556.3	289.5
1958	98.8	365.0	463.8	36.8	5.8	42.6	506.4	281.1
1959	137.7	514.0	652.0	32.2	7.8	40.0	692.0	414.3
1960	173.2	557.5	730.7	30.5	11.5	42.0	772.7	423.7
1961	188.6	542.7	731.3	35.2	12.5	47.7	779.0	334.1

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The market for phenol is dependent to a considerable extent upon the fortunes of phenolic resin manufacture, as indicated in Table 11. These resins account for roughly 60% of the phenol consumption. About one-third of all phenol produced is used as a chemical intermediate in the manufacture of alkyl phenols, bisphenol-A, polycarbonate resins and caprolactam. Phenol, in

the chlorinated form, is used in the manufacture of herbicides, the most important of which are 2,4-D and 2,4,5-T acid derivatives. The balance of phenol goes to the petroleum industry for solvent refining and additives and some for specialty products.

Table 11 - PHENOL END-USE PATTERN AS OF 1960

	<u>Percent of Total</u>
Phenolic Resins	58
Bisphenol-A	7
Caprolactam	7
Adipic Acid	6
Petroleum Solvent Refining	5
Pesticides	4
Alkylphenols	4
Miscellaneous (Aspirin, Polycarbonate Resins, Chlorinated, etc.)	9
	<u>100</u>

-9-

The actual production of phenol from 1950 through 1961 and estimated production through 1971 are shown in Figure 3. In 1961, 779 million pounds of phenol were produced with a predicted production of one billion pounds by 1965 and 1.4 billion pounds by 1971. If the present 85% ratio of production to capacity is maintained, 1,650 million pounds of phenol capacity will be needed at the beginning of the next decade.

E. Tar Bases

At the present time, petroleum sources are not utilized commercially for the production of tar bases, such as pyridine, picolines, pyrrole, quinoline, etc. The most important reason for not using petroleum sources is the absence of a substantial market. If such a market should develop, petroleum sources will undoubtedly be used. These sources should be considered as providing a large volume, low cost reactive hydrocarbon which can be converted into the desired tar bases. There are indications that various pyridines and indoles have attracted the attention of the petrochemical industry.^(5,6)

F. Miscellaneous Coal Chemicals

A number of sulfur and oxygen compounds derived from coal have presented interesting synthesis problems for the petrochemical industry. For example, considerable work has been done on the synthesis of thiophene using butadiene, butene and butane with sulfur and sulfur dioxide.^(7,8) Again, in this case, the raw materials derived from petroleum are available and can be used when a suitable market potential is developed.

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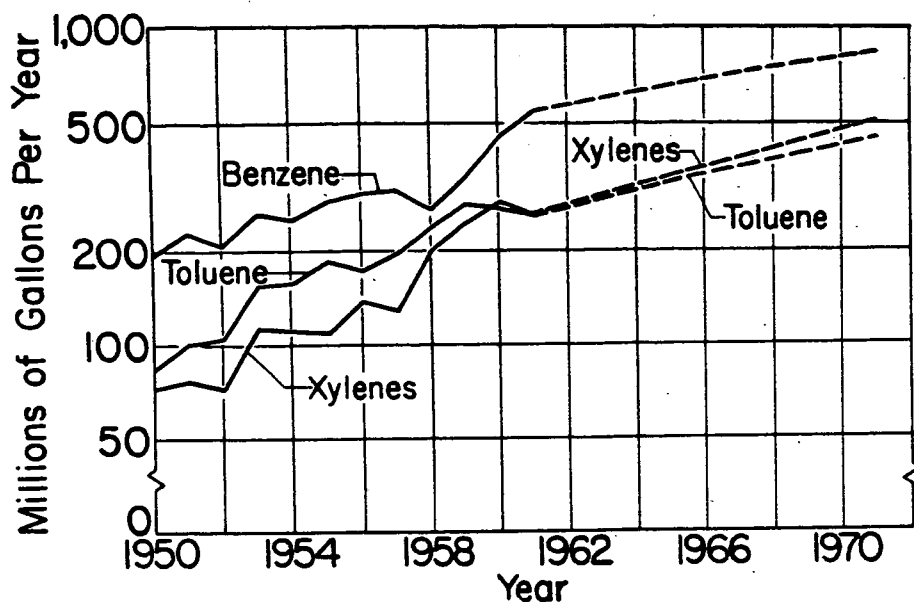
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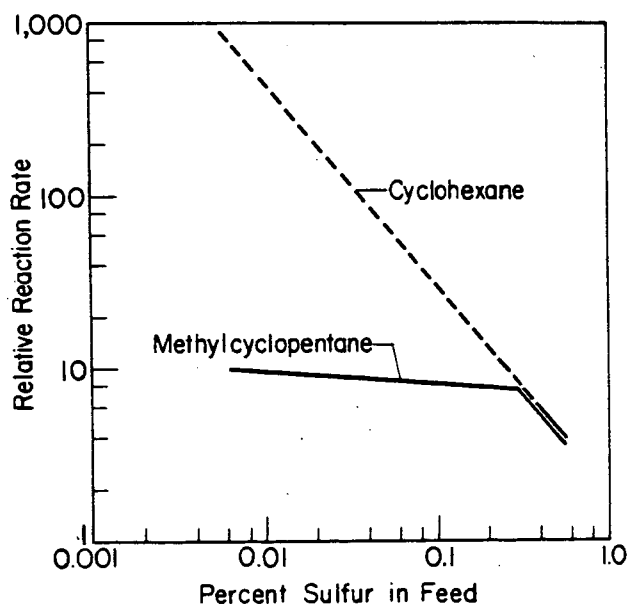
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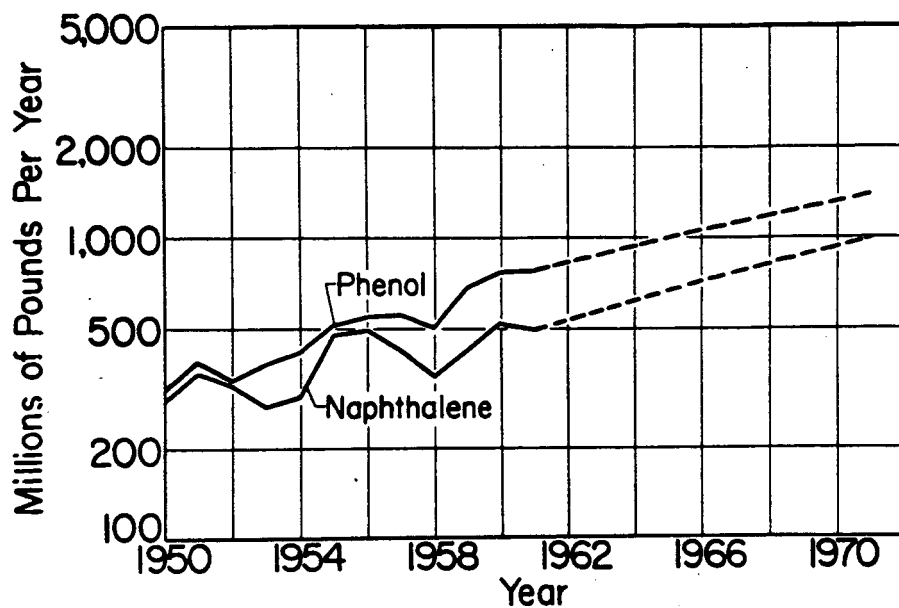
U. S. Tariff Commission
Stanford Research Institute
Oil Paint and Drug Reporter
Chemical Week
Chemical & Engineering News
World Petroleum
The Oil and Gas Journal



Benzene, Toluene and Xylenes Production
1950-1961 Actual - 1962-1971 Estimated
Figure 1



Effect of Sulfur on Conversion of Methylcyclopentane
and Cyclohexane to Benzene
Figure 2



Naphthalene and Phenol Production
1950-1961 Actual - 1962-1971 Estimated
Figure 3

Chemicals from Coal Hydrogenation Products

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INTRODUCTION

Coal has been the source of large quantities of useful chemicals and will continue to be for a long time to come. Because coal is a major resource of our country, the Federal Bureau of Mines is vitally concerned with its development and efficient utilization. Although millions of pounds of coal chemicals are marketed each year, people working with coal envision an even greater potential as new processes are developed. The discussion that follows will consider some of the methods that have occupied the minds of men for some time and some of the recent developments pioneered by the Bureau.

The coal hydrogenation process for making liquid fuels has been investigated in detail since its application as an industrial process almost 40 years ago. As time passed economic and technical changes have taken place that justify a reevaluation of existing knowledge. Under present quasi-peaceful world conditions where a copious supply of natural petroleum is available at low cost, hydrogenation of coal cannot be considered as a major source of liquid fuels.⁽⁵⁾ However, coal is an abundant raw material, and its application to other processes, exclusive of power and heat generation, presents a real challenge. Organizations in the United States and abroad have investigated the hydrogenation of coal and other coal utilization processes for many years. This work is still in progress in varying degrees, and in the following discussion are some of the gaseous, liquid, and solid chemicals that can be derived from the hydrogenation of coal. Associated with these technical developments are many design problems and an ever changing economic situation.

DISCUSSION

When considering the utilization of coal, it is natural to think in terms of thousands or even millions of tons a year. If the potential chemical products from coal are estimated, the quantities of chemicals must be evaluated in terms of present and potential markets. The tonnages of possible products are high and in some instances are greater than the current usage. Table 1 is a list of the more voluminous products that could be produced in a single 30,000-bbl/day coal hydrogenation plant that reacts about 12,000 tons of coal per day. These facts are fairly well known, and rather than recite comparative figures, consideration will be given to some of the more plentiful chemicals. It should be mentioned that there is considerable process flexibility to change the product distribution.

The potential yield of most chemicals from hydrogenation is several times greater than from carbonization since most of the carbon is converted to liquid and gaseous hydrocarbons. The list of potential chemicals from coal hydrogenation is extensive and generally can be categorized by the type of compounds shown in figure 1. Products of coal hydrogenation contain appreciable quantities of aliphatics, aromatics (single-ring and polycyclic), substituted aromatics, heterocyclic compounds, and hydroaromatics. Many of the products that can be produced in quantity have only limited markets, and their disposal could be a problem.^{(4), (7)}

TABLE 1.- Chemicals from a Coal Hydrogenation Plant
(30,000 barrels per day from Illinois coal)

<u>Aromatics</u>		<u>Million pounds per year^{a/}</u>
Benzene	224	(4,000) ^{b/}
Toluene	372	(1,875)
Xylene	425	(1,880)
Ethylbenzene	73	-
Naphthalene	104	(497)
Mixed aromatics	<u>175</u>	
Total	1,373	
 <u>Tar acids</u>		
Phenol	51.8	
o-Cresol	5.8	
m-, p-Cresol	63.3	
Xylenols	<u>44.8</u>	
Total	165.7	
Ammonium sulfate, tons/year ...	148,500	
Sulfuric acid, tons/year	29,400	

a/ 330 stream days.
b/ 1961 production from all sources in parentheses, million pounds per year.

It would be desirable to be able to produce and separate only compounds for which there is a ready market. In this way, salable products would not have to bear the burden of chemicals that have only fuel value.

At the present time the most useful products from coal are the low-molecular-weight members of each series; benzene, toluene, xylene, naphthalene, and phenol. These are the preferred elementary building blocks used to make well-defined products. Plastics, synthetic fibers, resins, detergents, and elastomers consume 7.3 billion pounds a year of benzene, toluene, and xylene, 520 million pounds of naphthalene, and 780 million pounds of phenol. The consumption of these five major raw materials that can be made from coal is still growing. So far, no one has been able to justify the investment in a coal hydrogenation system to produce the few marketable products. In fact, the direction in recent years has been to dealkylate substituted aromatics from petroleum, producing benzene and naphthalene for consumption in synthesis industries.⁽¹⁾ Here is a case where knowledge of the product composition and process know-how were applied to supply a need as the market developed beyond the capacity of the primary sources.

In 1952 Chemical and Engineering News⁽³⁾ described studies by Carbide and Carbon Co. and its "coal hydrogenation unit designed to manufacture aromatic chemicals." Carbide and Carbon did much work on the primary liquefaction products and found a large number of chemicals worth up to several dollars a pound. Some of the products visualized as finished products of intermediates were the light products B-T-X, naphthalene, and tar acids and heavier useful materials such as indan, fluorene, anthracene, phenanthrene, indanols, quinoline, carbazole, furans, and many others. These are indicated in the figure described previously. Markets have not developed for most of the high-molecular-weight products that could be separated. Instead, the demand continues to increase for lower-molecular-weight chemicals as monomers for designing complex molecules that have no structural counterpart in the hydrogenation products.

Condensed aromatic structures such as pyrene and coronene, which may be considered as useful products, are resistant to mild hydrogenation conditions. They are recovered in the heavy oil product from hydrogenation of coal and can be isolated in a crystalline form. The greatest amount of condensed aromatics are recovered in "kiloil" produced by roasting the plant residue. Actually, condensed aromatics are formed in the kiln through cracking and dehydrogenation during carbonization. Other components of the recovered oil are methylpyrenes, carbazole, and some 1,12 benzperylene.

Pyrene, which may be in 10 to 12 percent concentration in the kiln oil, can be concentrated further by distillation and isolating the mid-40-percent fraction. Carbazole is concentrated in the low-boiling fraction, and the vacuum residue contains the coronene concentrate. The pyrene fraction is distilled into narrow fractions separated from the oil and mixed with a solvent such as benzene-alcohol that dissolves only oil. When the solvent is centrifuged or filtered off, pure pyrene remains.

Carbazole is very resistant to hydrogenation, and most other aromatics in the low boiling fraction of the kiln oil can be hydrogenated to lighter distillable oils. The remaining carbazole is insoluble and can be separated by filtration and distillation.

Coronene can be isolated from the kiln oil residuum after vacuum distillation to remove pyrene. The fraction boiling at 350° to 400° C is slurried with benzene and filtered. Coronene is insoluble and is recovered in pure form. Contaminating hydrocarbons can be hydrogenated to lower boiling liquids by catalytic refining. Coronene is not hydrogenated and is recovered as a precipitate. Further purification can be done by vacuum distillation or recrystallization from o-dichlorobenzene.

Small-scale studies on the hydrogenation of coal have been limited in the past by the relatively long time, 3 to 4 hours, required to heat and cool in autoclave. The influence of temperatures, especially above 350° C, on the experimental results has always raised questions concerning the validity of the data. The reaction system shown in figure 3 was developed with two main objectives, rapid heating and cooling and small charge size. Passing a low voltage and high current (about 700 amps at 15 v) through the type 304 stainless steel reactor raises the temperature to 800° C in about 2 minutes. Pressures as high as 6,000 psig could be maintained for over an hour before metal fatigue occurred. When an experiment is completed, the reactor is cooled in about 10 seconds by a water jet. Details of this apparatus have been published.⁽⁹⁾ Experiments on the hydrogenation of coal could then be made at more severe conditions for the production of methane and light hydrocarbons, and from these studies a new synthesis of polycyclic aromatics was found.

If dry coal is hydrogenated at 6,000 psig and 800° C for zero and 15 minutes and a hydrogen rate of 100 scfh (0.5 fps), the results shown in figures 4 to 6 are obtained.⁽⁸⁾ In general, the conversion of all coals is most rapid within the first 3 minutes and thereafter proceeds at a steady, slower rate. The yield of gas is similar but there is no change in the yield of liquids which are produced in the early stage of the reaction and swept out of the apparatus. This reaction is substantiated by the comparative experiments shown in figure 7, where two sets of experimental data made at two gas velocities are shown. At the lower gas rate of 20 scfh the hydrocarbon vapors have more time to be hydrocracked to additional hydrocarbon gases.

The concentration of methane in the C₁ to C₃ fraction of the gas calculated from the spectrometer analyses increased with coal rank as shown in table 2. Although the gas formed from low-rank coals contained less methane, there were more higher hydrocarbons present which gave a higher heating value. This trend extends to the oils produced; that is, the low-rank coals produced more liquid product as shown in figure 6. Anthracite and char produced no liquid products.

TABLE 2.- Distribution of light hydrocarbons in the gas

	Composition, vol pct		
	Methane	Ethane	Propane
Lignite	82	15	3
High volatile C	88	10	2
High volatile A	90	9	1
Anthracite	92	7	1
High volatile C char ..	92	8	0

An analysis of the liquid product from a Wyoming coal (hvcb) is shown in table 3. The mass spectrum indicates a complex mixture of products containing aromatics and tar acids. Analyses of the liquids from lignite and Pittsburgh seam coal (hvab) were almost identical to the results shown for the hvcb Wyoming coal.

TABLE 3.- Mass spectra of oils from hydrogenation of a Wyoming coal (hvcb)
(6,000 psig, 800° C)

Possible compound types including alkyl derivatives	Volume-percent of total oil
Benzene, toluene, etc.	23.1
Phenols	21.5
Naphthalenes	18.7
Indanols	11.0
Phenanthrenes, anthracenes ..	3.3
Balance	22.4

The next subject describes some work that falls in the category of unexpected findings. When anthracite coal was hydrogenated for making high-Btu gas, the cold trap contained a yellow powder identified by ultraviolet analysis as a high concentration of coronene.

The experimental data shown in table 4 indicate the limits for temperature and pressure - 6,000 to 8,000 psig and 700° to 800° C. The maximum yield of coronene was 0.8 wt pct of the low-volatile (4.2 percent volatile matter) anthracite. The product was a low-density, porous yellow-orange solid that was about 70 percent coronene by ultraviolet analysis. Some samples contained over 80 percent coronene. The balance is mostly 1,12-benzperylene and pyrene. Most of the coronene was recovered in the cold trap, but some was obtained from the connecting lines and reactor by washing with warm benzene. Coronene in the wash is included in the yield.

TABLE 4.- Coronene from hydrogenation of anthracite

30 minutes at -		Coronene, weight-percent	
Temperature, °C	Pressure, psig	In solid product	Of maf coal
600	6,000	0	0.01
700	6,000	71	0.5-0.8
800	6,000	37	0.3
600	8,000	0	0
700	8,000	49	0.5-0.7
800 ^{1/}	8,000	38-54	0.4-0.5
700	3,000	50(est)	0.08

^{1/} 15 minutes.

Coronene could also be produced from Pittsburgh seam coal (hvab), but from the few experiments made it appeared that the higher temperature of 800° C at 6,000 psig was required to yield the same amount of coronene - about 0.5 wt pct of the maf coal. However, no dry solids were recovered in the cold trap, and the yields are based on an analysis of the benzene washings. Equal quantities of coronene and pyrene were found when a hvab coal was used.

Other materials such as asphaltenes and centrifuge residue from the hydrogenation of coal were also examined. The yields of coronene were lower and 4 to 10 times more pyrene were present. Thus, no other coal or coal hydrogenation product was as good as anthracite for this synthesis. Since the yield of coronene from coal is only 0.5 to 0.8 percent, a use must be found for the resulting hydrocarbon gases and char. It has been estimated that if the gas and char are sold for fuel value, the coronene could be sold for less than \$1 a pound.

Another product that can be considered is the mixture of closely related chemicals that may be used as fuel for supersonic aircraft. The distillable oil from the hydrogenation of coal contains bicyclic aromatics that could be hydrogenated to naphthenes that are thermally stable and have many desirable properties. An oil produced in the pilot plant of the Bureau of Mines was distilled to 325° C end point oil for feed stock. This oil was then desulfurized and partially hydrogenated over cobalt-molybdate catalyst at 2,500 psig, 400° C, 50 scf H₂ per pound of oil, and at a space velocity of 3 vol oil/hr/vol catalyst. A 180° to 280° C fraction of the desulfurized oil was saturated over a nickel catalyst to produce a naphthenic product.

A similar fuel for supersonic jet aircraft has been produced from a distillable fraction of tar made by low-temperature carbonization. Results of this work have been published in a Report of Investigations.⁽¹⁰⁾ In figure 8 the narrow distribution of products indicated by mass spectrometer analysis is shown. Practically all of the oil is in the C₁₀ to C₁₅ range with a maximum at C₁₂ or C₁₃. This fuel met all but one of the specifications established tentatively for this type of fuel. For some as yet unexplained reason, this oil was not stable in the high-temperature test unit. However, recent laboratory tests indicate that the oil is more stable after rehydrogenation.

A plasma jet unit is now being used for experiments with coal at very high temperatures. If the temperature of the coal approaches the plasma temperature, extremely severe hydrogenation conditions can be established.

At the present time only limited results are available. When coal is heated in an argon plasma, the products are a very fine residue, carbon monoxide, methane, acetylene, hydrogen, and nitrogen. The composition shown in table 5 was obtained with slow cooling of the products. Quenching with gas or liquids will give other products. Also, the products will vary with other operating variables such as the working gas composition, gas and coal rates, and power input.

Other forms of energy such as microwaves, corona discharge, and maser and laser beams have also been considered as an active environment for coal hydrogenation experiments. However, manpower and financial limitations are keeping these in the paper stage at the present time.

Several important factors are becoming evident as work on hydrogenation of coal continues. The system is being modified to yield fewer products. Instead of a wide range of liquid fuels we have been making hydrocarbon gases and light aromatics, relatively pure polycyclic products, and relatively narrow fractions. Hydrogenation yields more of these desired products than a carbonization or coking process. Thus, hydrogenation provides us with a potential for providing large quantities of useful products when a profitable demand develops. Many people envision a coal hydrogenation product "tree" as extensive as the popular "tree" published for coal tar. The Bureau of Mines will continue to do its part in providing an atmosphere in which the hydro-

genation tree will come to fruition.

TABLE 5.- Gas composition from coal in a plasma jet
(5 kw net power input, hvab coal 70 x 100 mesh)

Argon	84.5	-
Hydrogen	9.3	60
Nitrogen	0.9	6
CH ₄	0.3	2
C ₂ H ₂	2.3	15
CO	2.7	17
CO ₂	tr	-

Coal conversion - 15 percent

Residue (<325 mesh) - 6 percent of coal feed

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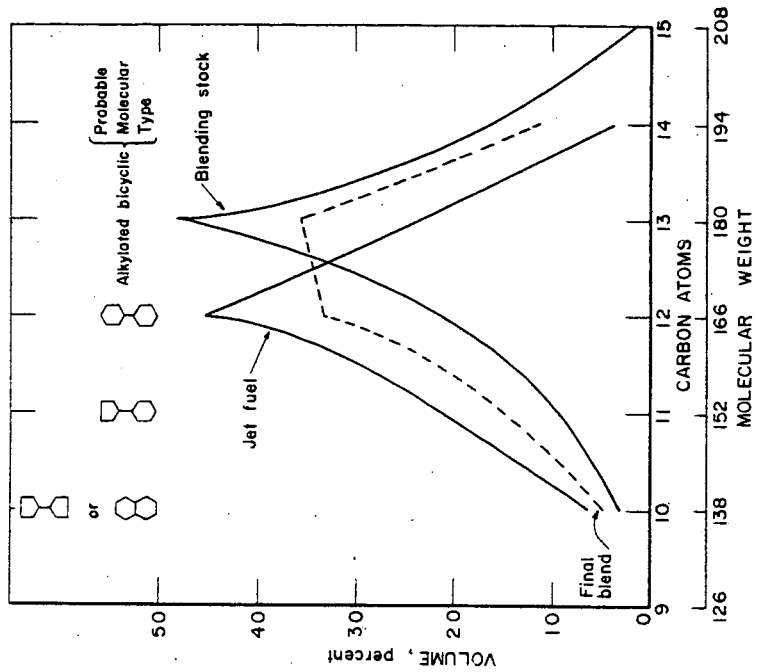
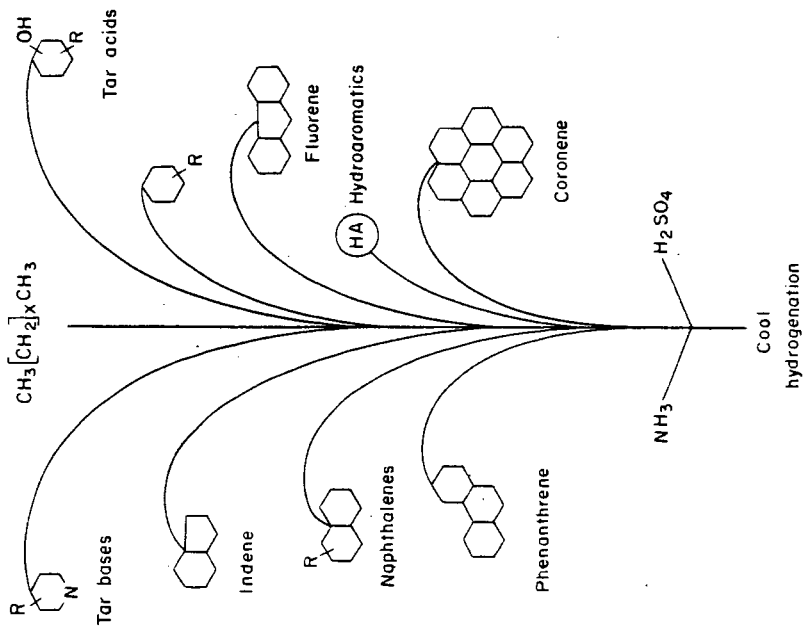


Figure 8.- Molecular weight distribution in jet fuels.

Figure 1.- Typical chemicals from hydrogenation of coal.

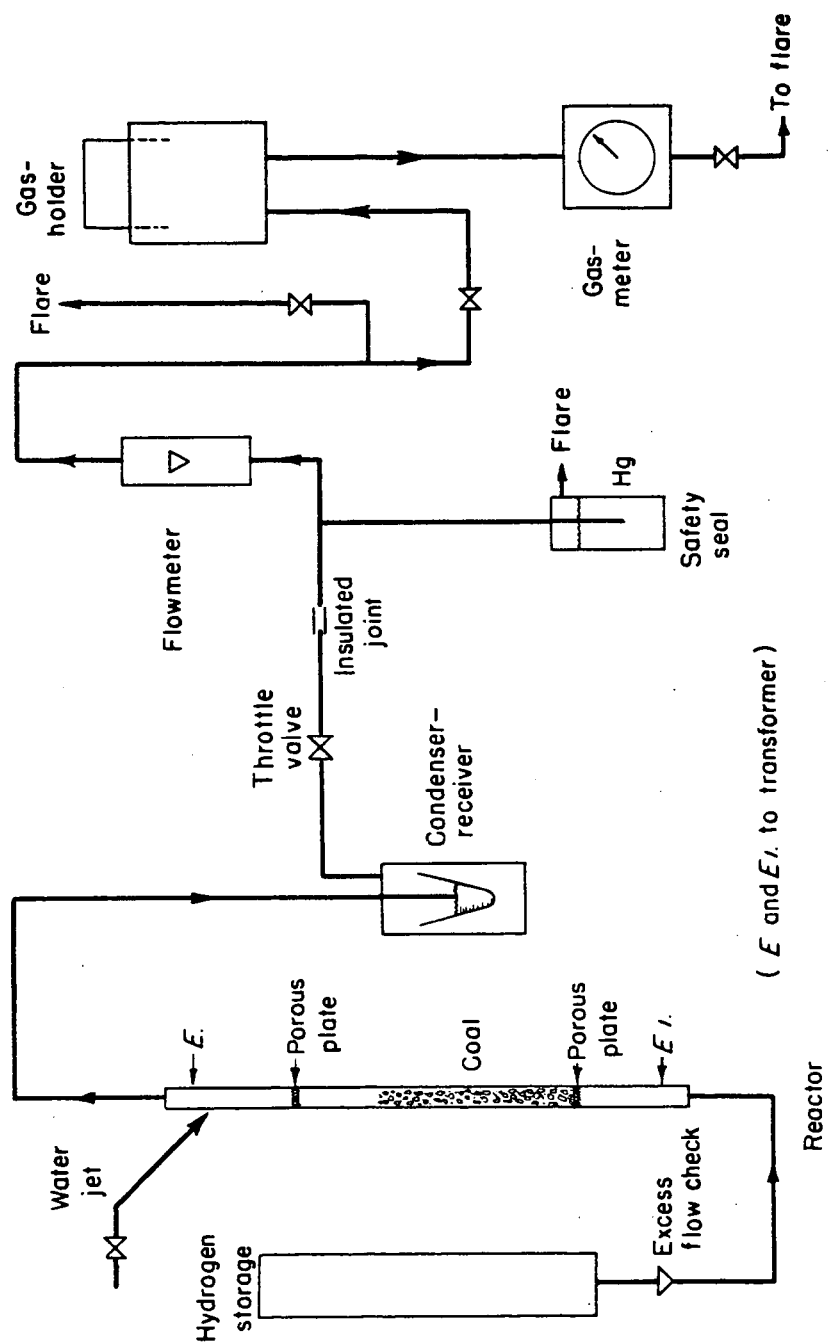


Figure 3.—Simplified flow sheet of apparatus.

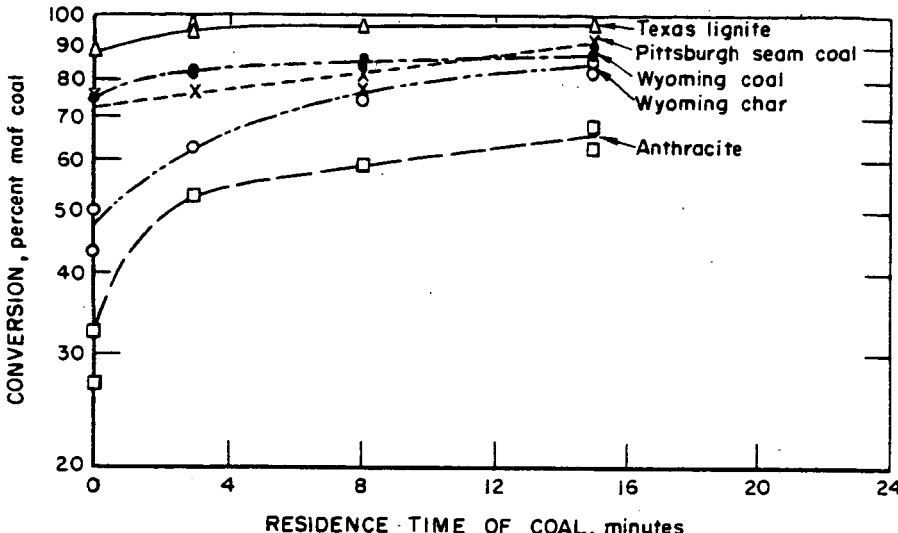


Figure 4.- Effect of residence time on conversion.

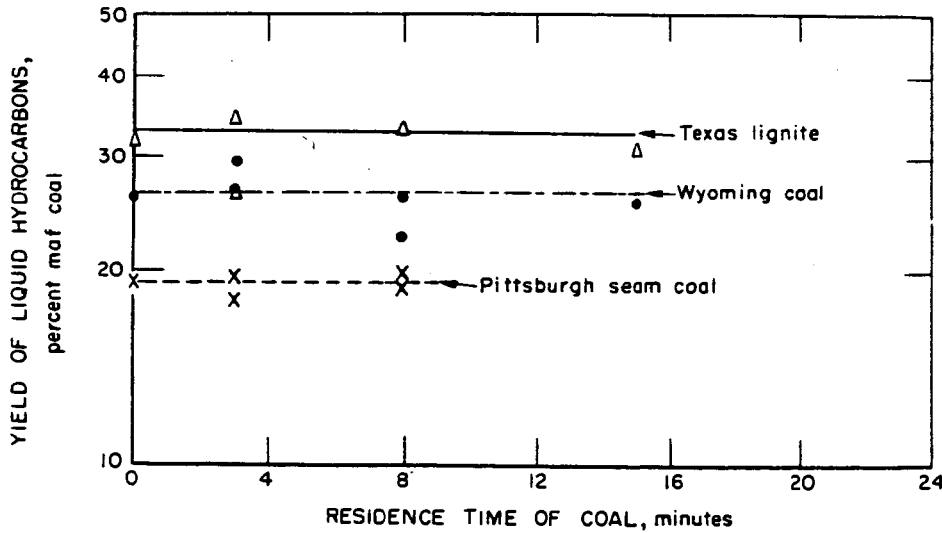


Figure 6.- Effect of residence time on yield of liquid hydrocarbons.

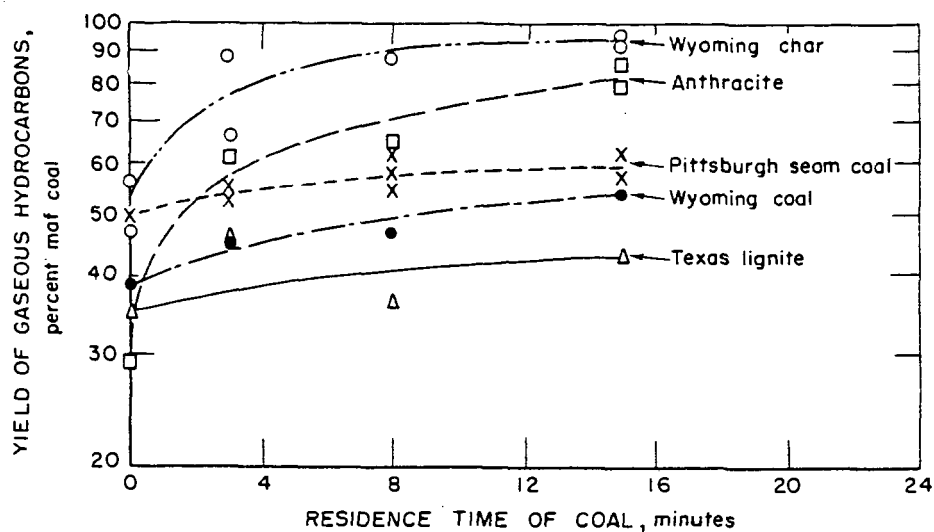


Figure 5.—Effect of residence time on yield of gaseous hydrocarbons.

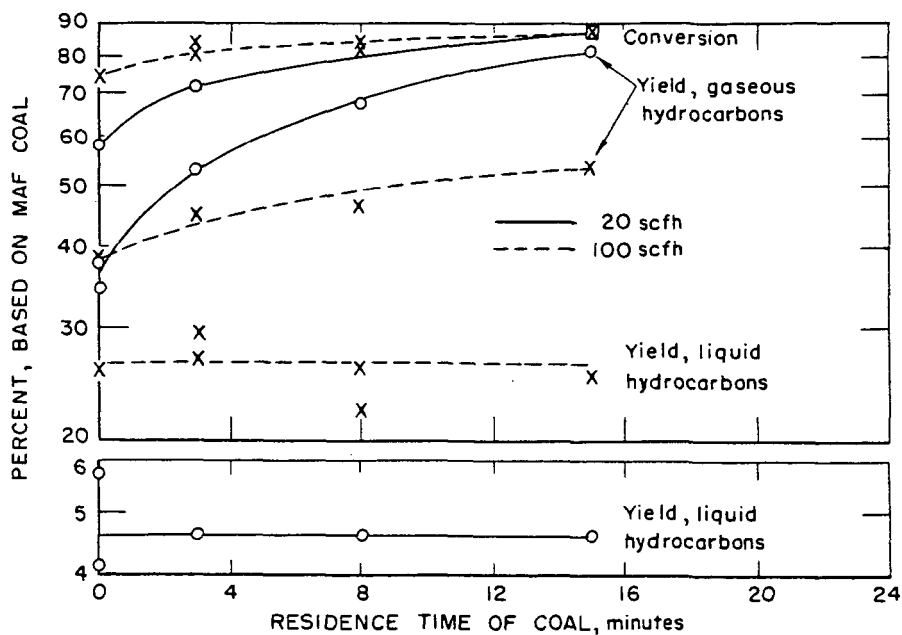


Figure 7.—Effect of residence time on product distribution for Wyoming coal at two gas rates.

COAL CHEMICALS FROM COAL OXIDATION PRODUCTS

R. S. Montgomery

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Coal can be oxidized in various ways to yield mixtures of organic acids. The product obtained, of course, depends to some extent on the specific process. The process that The Dow Chemical Company has felt to be the most promising involves the oxidation of a suspension of bituminous coal in aqueous sodium hydroxide by means of gaseous oxygen under high pressure. This process requires about three pounds of sodium hydroxide for every pound of coal oxidized. The Dow Chemical Company as you know is a large producer of chlorine and sodium hydroxide. Since we have large internal requirements for chlorine without the equivalent requirements for the sodium hydroxide produced as a co-product, this process would seem ideal for us. The process that we used is basically the process developed by The Coal Research Laboratory of The Carnegie Institute of Technology.¹ We did, however, refine this process somewhat by using a more sophisticated, multiple-chamber, stirred reactor so that the process could be carried out continuously. The Coal Research Laboratory had used a simple stirred autoclave, but of course recognized that this reactor would probably be modified to allow continuous operation in an actual commercial process.

The oxidation products obtained by this process are sodium carbonate, a relatively small amount of the base-soluble, water-insoluble, humic acids, and the most important product, a light-yellow colored, water-soluble mixture of aromatic acids. The average molecular and equivalent weights of these so-called "coal acids" are about 270 and 82 respectively, resulting in an average carboxylic acid functionality of 3.3. The main components of this mixture are the various benzene, naphthalene, and biphenyl polycarboxylic acids; 1,2,4 benzenetricarboxylic acid, which constitutes about 21% of the mixture, is the most important single component.^{2,3,4,5} The separation or even fractionation of this mixture is difficult and expensive⁶ and so any commercial use for it will probably, at least initially, be a use for the mixture as a whole without any extensive separation.

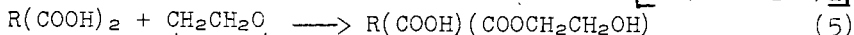
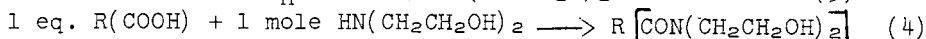
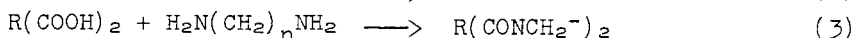
There are many potential uses for the coal acids, and some of them appear to have a great deal of promise. This product is quite unique in that these acids are almost completely aromatic but have sufficient polyfunctionality so that they are readily soluble in water, and instead of crystallizing, form an amorphous film on the removal of the water. This great difference between the coal acids and currently available aromatic acids is both a strength and a weakness. It is a strength because there is the possibility that very large amounts could be required for applications where virtually no substitutes could be found. It is a weakness in that there is no ready-made market for a material of this kind, and it is difficult to assess accurately the volume that could be sold and the value that it would have to the consumer.

The acids themselves and their salts have been suggested as substitutes for other water-soluble acids in various applications,¹ and in addition

have been used as corrosion inhibitors⁷ and as a set retarder for gypsum⁸. One application for these acids that is certainly not obvious is their use as a warp size for synthetic fibers. The coal acids were found to be an excellent warp size for nylon, polyester fibers, and cellulose.^{9,10,11} The reason for this is that these polyfunctional acids interact more and more strongly by hydrogen bonding as their aqueous solution becomes more and more concentrated until finally they form, to all intents and purposes, a "high polymer" at very low water contents. These crosslinking hydrogen bonds are cleaved by water and so this "high polymer" is still perfectly soluble in water. Although the coal acids make an excellent warp size, they do have a very real disadvantage. Textile mills are naturally reluctant to use a colored size on an expensive fiber even if they are assured that it can be entirely removed after weaving.

Perhaps the most obvious derivatives of an organic acid to be investigated are the esters, and it was found that the various esters of the coal acids could be used as plasticizers,¹ synthetic lubricants,¹² hydraulic fluids,¹³ and corrosion inhibitors.¹⁴ Here again their color mitigated against their use in plasticizers and they did not possess any property, including potential price, that would make them extremely interesting for these applications. If they were available there would doubtless be some sold for these purposes, but a production plant would not be constructed on the strength of these applications.

The most promising application for the coal acids is their use in thermosetting resins. They can be reacted with an alkanolamine,¹⁵ alkylene oxide, polyhydroxyl compound¹⁶, or polyamine¹⁷ to give a wide spectrum of resins with varying properties. The polyamide, polyester, or combination of functional groups possible in these resins are illustrated in the following examples:



It is advantageous to prepare a partially cured but still water-soluble resin. Heating equivalent amounts of the coal acids and monoethanolamine at 170°C. for 3 hours gave 85% esterification, but very little amide formation. Other partially cured but water-soluble resins can be prepared by heating the coal acids with pentaerythritol, or ethylene, propylene, or butylene oxides. These partially cured resins are in the form of viscous aqueous solutions. They can be stored indefinitely in this form without any danger of further polymerization. This partially cured material will completely cure to a strong, insoluble, crosslinked structure when it is heated at elevated temperatures (over 200°C). In addition, these partially cured coal acid resins are compatible with the water-soluble phenol-formaldehyde prepolymers, and are incorporated in the phenol-formaldehyde polymer structure. The physical properties of the cured coal acid resins compare favorably

with those of other thermosetting resins, and in addition at a suitably large volume their cost should be less than the other thermosets.

These coal acid resins could be used for many purposes such as plywood, hardboard, and chipboard binders¹⁸, binders for fiberglass, and shell molding and foundry core resins¹⁹. There has been a great deal of work done especially in the field of foundry resins, and these resins have shown considerable utility. The extremely long pot life is a definite advantage for many uses, but the attendant relatively high curing temperature is a disadvantage when the resin is used to bind thermally sensitive materials. In any case the coal acid resins are very promising and appear to represent the best possibility for a large-scale use for the coal acids.

The final portion of my talk will be concerned with the question of the economics of producing a product such as this and why The Dow Chemical Company has not begun commercial production. Basically, the coal acids are a low-priced product. If they are to be commercially successful they must compete pricewise with the products which will do a similar job in a particular application, and in general these are high-volume, relatively low-priced chemicals. In addition to being a low-priced product, the coal acids also require a large capital expenditure for production facilities. For a product of this kind requiring a large capital expenditure, there is a characteristic volume-cost curve. At high production rates the cost is low, but where a high production rate is not justified, the product is very expensive to produce. Therefore a company embarking on the commercial production of a product such as this must take a calculated risk and construct a large production plant and price the product low in the hope of developing a large market for it which will justify this large plant and low price. If the market does not develop as hoped, a great deal of money could be lost. Therefore, what is needed to stimulate interest in the commercial production of coal chemicals from coal oxidation products is a single large-scale use which seems certain enough to justify the construction of a large production plant. At the present time the coal acid resins appear to represent the best possibility of obtaining this large-scale use.

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INDENOLS IN COAL TARS. THE FIRST PREPARATION OF INDENOL.

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Indenes have long been known to be major constituents of coal tar, but only recently evidence for the presence of indenols has come from examination of several coal tars by low ionizing voltage mass spectrometry.^{1/} This evidence is based on the appearance of a series of peaks at mass units corresponding to the molecular weights of indenol and its homologues in coal tar phenolic fractions. This series of peaks parallels the corresponding indanol series of mass unit peaks. These ubiquitous but elusive compounds may be responsible for much of the gum formation in coal tar, particularly in the tar acid fraction.

The parent hydrocarbon, indene, has been a chemical of commerce for several years, and recently a series of indene derivatives has been made available for development purposes. The commercial importance of these compounds stems from their high chemical reactivity. In the case of indenols, which appear to be major components of certain coal tars, the presence of a phenolic group as well as an olefinic bond in conjugation with an aromatic ring would be expected to provide even greater opportunity for reaction.

While indene and several of its derivatives are thus readily available, indenols have escaped both synthesis and isolation. Two derivatives of indenol, an indenol-O-acetic acid^{2/} and a methoxyindene^{3/} have been reported in the literature, but no reference exists for any preparation of the parent phenol. It should be pointed out that 1-indenol is known, but this compound is not phenolic.

In order to study the properties of the indenols, and even to prove their presence in coal tar, it appeared necessary to first isolate or synthesize at least one member of the series. The synthetic approach proved to be more rewarding.

We have now developed a successful procedure for preparing both 4- and 5-indenol by catalytic dehydrogenation of the respective indanols which are available from coal tar. Initially, a procedure developed by Webb and Corson^{4/} for the dehydrogenation of substituted ethylbenzenes to the corresponding styrenes was adapted. The method involves passing steam and indanol over a chromia-alumina catalyst at 570° C. The procedure was not always reproducible, and analysis of the product by mass spectrometer and gas chromatograph showed that unchanged indanol was usually the major constituent.

Subsequently, this procedure was modified, resulting in higher and more reproducible yields. In addition, several techniques have been developed for purifying the product. In the dehydrogenation itself, nitrogen has been substituted for steam as a carrier gas. The pyrolysis temperature has been increased to 650° C. In this way, we have succeeded in preparing sizeable quantities of indenols in good yields from both 4- and 5-indanol. The same procedure has been used to dehydrogenate indanol trimethylsilyl ethers to the corresponding indenol trimethylsilyl

ethers. This latter method is more convenient, since the trimethylsilyl ethers are liquids and thus more readily fed to the pyrolysis column. In addition, the ethers give somewhat better conversions to the dehydrogenation product and appear to be more stable during storage. Gas chromatography of the indenols as their trimethylsilyl ethers has certain advantages. In general, the ethers can be chromatographed at lower column temperatures than the parent indenols. The non-polar nature of the ethers is an additional advantage, allowing a wider choice of column packing and giving better separation and less tailing of peaks.

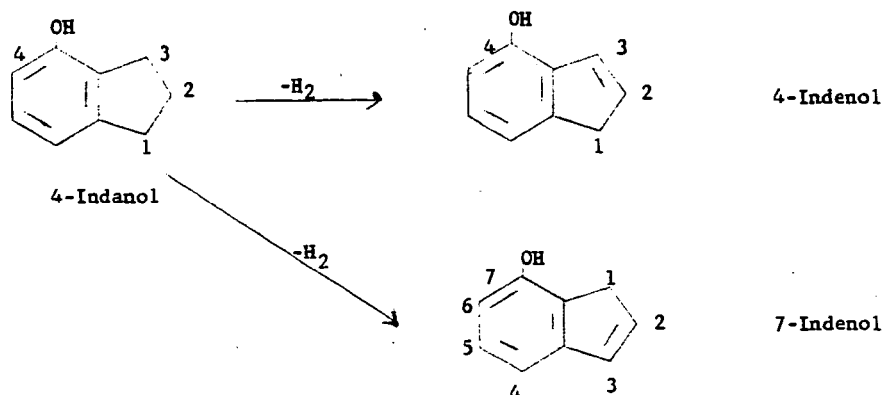
Both the indanol and indenol trimethylsilyl ethers are readily prepared by refluxing the phenols with hexamethyldisilazane,^{5/} and the indenols are easily regenerated from the ethers by refluxing with ethanol.

The initial isolations of pure indenols required repeated recrystallizations from petroleum ether to obtain pure, indanol-free samples. Purity was readily determined by gas chromatographic analysis, and checked by low ionizing voltage mass spectrometry which gives a measure of the ratio of mass 132 (indenol) to 134 (indanol).

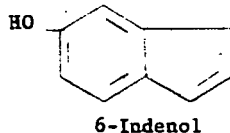
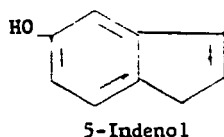
Subsequently, several chromatographic procedures were developed which allowed cleaner separation of indenol from indanol. The first chromatographic separation was carried out using a glass column packed with Chromosorb on which was adsorbed aqueous AgNO_3 solution.^{6,7/} Crude indanol-indenol pyrolyzate mixtures were dissolved in heptane and put on the column. Elution with more heptane removed only indanol. The indenol was eluted with methyl isobutyl ketone.

The second, more efficient chromatographic separation was a similar procedure, called "ligand exchange."^{8/} This procedure combines ion exchange and coordination chemistry to accomplish a task that neither could do alone. An ion exchange is prepared from an ion exchanger resin and a suitable metal ion (in this case Ag^+) which can complex with the appropriate ligand (in this case an olefin). In the procedure used, a Dowex cation exchanger resin was washed with an aqueous solution of silver nitrate and then air-dried. The silver impregnated resin was packed into a chromatographic column and an indanol-indenol mixture in acetone poured onto the column. Elution with petroleum ether removed the indanol. The indenol was eluted with chloroform. When the column was deliberately overloaded with indenol, the excess came off with the indanol, resulting in pure (99+ percent) indenol in the chloroform eluate. This proved to be the best way to obtain analytically pure indenol samples.

The initial gas chromatographic analysis of the indenols was used to determine ratios of indanol to indenol in pyrolyzate products and later in purified material. It was evident at an early stage of this problem that dehydrogenation of an indanol did not produce a single product, since the indenol peak on a gas chromatogram was readily resolved in each case into two peaks. The dehydrogenation product from 4-indanol was separated on a column to give two different peaks, which have the same mass and almost identical ultraviolet spectra. It is believed that these two compounds are the isomers, 4- and 7-indenol, both of which can be formed by dehydrogenation of 4-indanol.



The ease with which these two compounds isomerize is not known. However, the individual isomers appear to be stable with respect to each other, since freezing out a given isomer and re-injection in the column fails to show any evidence of isomerization of the given material. This isomeric pair phenomenon also has been found in the product of dehydrogenation of 5-indanol. The 5- and 6-indenol so produced are less readily separated by gas chromatography (Figure 1).



Ingold,^{3/} in his investigation of the 5-(6-) methoxyindenes, came to the conclusion that the material behaved as though it were a mixture of the two isomers. Wheland^{9/} has referred to the compounds as tautomers. However, this is based on observations of experiments which could have given rise to isomerization. Whether true tautomerism exists has yet to be demonstrated. In fact, the gas chromatographic behavior reported here implies a stability great enough to deny the title of tautomers to these pairs of isomers.

Various spectral techniques have been applied to this problem to verify the structure of the indenols. The nuclear magnetic resonance spectra of both indenol samples is consistent with the proposed formulas in that there are two olefinic hydrogens having the same chemical shift as those in indene.^{10/} Ultraviolet spectra of the indenols and their trimethylsilyl ethers bear the same relationship to the spectrum of indene as do those of the indanols and their trimethylsilyl ethers to the spectrum of indane. The infrared spectra of the samples are consistent with indenol structures.

EXPERIMENTAL

The 4- and 5-indanols used in this work have been obtained from Aldrich Chemical Co. and Rutgerswerke A. G. (Germany).

Design of Pyrolysis Column

The column used for dehydrogenation of indanols is a stainless steel tube, 100 cm. long, with an O.D. of 25 mm. The lower 90 cm. of the tube is wrapped with 33 feet of #20 B&S nichrome wire covered with porcelain insulator beads. The furnace portion

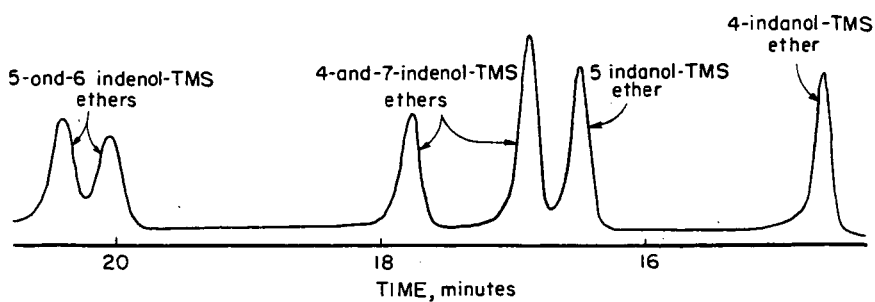


Figure 1.—Gas chromatography on a capillary column of a mixture of trimethylsilyl ethers of indanols and indenols

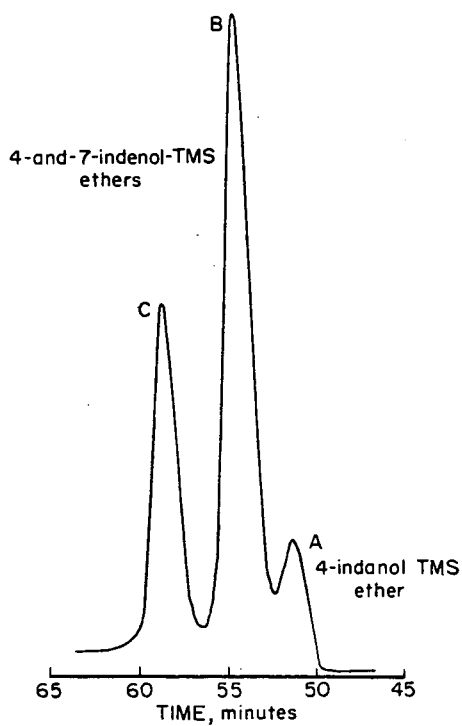


Figure 2.—Gas chromatography on a packed column of indanol-indenol mixture, as trimethylsilyl ethers.

of the tube is jacketed by a piece of asbestos pipe insulation. To the bottom of the tube is welded an outlet tube of 8 mm. O.D. stainless steel leading to one or more cold traps by means of rubber tubing. The top of the column has a rubber stopper containing a needle-valve controlled addition funnel, a stainless steel thermocouple well extending approximately 50 cm. into the tube, and a hypodermic needle for admitting nitrogen. The packing consists of a lower layer (10 cm.) of glass beads, a layer of catalyst approximately 60 cm. in length, and a top layer of glass beads. Preheating tapes are wound around the top 10 cm. of the tube and also around the addition funnel.

Preparation of Catalyst

A solution of 225 grams of ammonium dichromate and 450 grams of aluminum nitrate nonahydrate in 1500 milliliters of distilled water was warmed to 80° C. Ammonium hydroxide was added until precipitation was complete. The precipitate was filtered and dried at 110° C and then decomposed at 500° C. The powder was pelleted with 4 percent aluminum stearate to 1/8-inch diameter pellets. The catalyst was activated by heating to 570° in a stream of air.

Preparation of 4-Trimethylsiloxylindane

A solution of 20 grams of 4-indanol in 30 milliliters of hexamethyldisilazane was refluxed overnight under nitrogen. The excess hexamethyldisilazane was removed by distillation and the trimethylsilyl ether distilled under vacuum (bp 86-88 at 5 mm.).

Dehydrogenation of 4-Trimethylsiloxylindane

While a stream of nitrogen was flowing through the pyrolysis column, 30 grams of 4-trimethylsiloxylindane was allowed to drip onto the column at a rate of 30 grams per hour. The column temperature was kept at 650° C. The product was collected in three traps, the first of which was cooled in acetone/dry ice and the other two, which contained a mixture of benzene and petroleum ether, were cooled in ice water. The solvent was evaporated from the combined trap contents to yield over 25 grams of crude product. Gas chromatographic examination showed the presence of some 4-indanol (as its trimethylsilyl ether) as well as traces of solvent. The major portion of the material appeared to be 4- and 7-indenols (as their trimethylsilyl ethers). This was confirmed by mass spectrometric analysis.

A portion of the crude indenol trimethylsilyl ether was refluxed overnight in ethanol to hydrolyze it to the indenol. The indenol was recrystallized from carbon tetrachloride and from petroleum ether to give needles, mp 77.5-79° C. Calcd. C_9H_8O : C, 81.79; H, 6.10. Found: C, 82.07; H, 6.46.

A sample of this indenol was converted to its trimethylsilyl ether for gas chromatographic analysis. This showed the complete absence of indanol. Two gas-chromatographically separable components were present in a ratio of about 4 to 1.

Dehydrogenation of 5-Trimethylsiloxylindane

In a similar manner, a mixture of 5- and 6-trimethylsiloxylindane, having a gas chromatographic peak ratio of 4 to 3, was prepared by dehydrogenation of 5-trimethylsiloxylindane (bp 97-99 at 6-7 mm.). The material was converted by refluxing in ethanol to the indenol, mp 78-79.5° C. Calcd. for C_9H_8O : C, 81.79; H, 6.10. Found: C, 81.92; H, 6.20.

Dehydrogenation of 5-Indanol

While a stream of nitrogen was flowing through the pyrolysis column, molten 5-indanol was dripped onto the column at a rate of 30 grams per hour with the column temperature at 650° C. The product was collected in an ice cooled trap. Gas chromatographic examination of the trimethylsilyl ethers of the product showed it to be largely 5- and 6-indenols.

Figure 1 is a chromatogram of a synthetic indanol-indenol-TMS ether mixture run on a 150-foot x 0.01-inch I.D. capillary column coated with Ucon LB-550-X (a polyalkylene glycol containing an oxidation inhibitor). This capillary column is mounted in a Perkin-Elmer 154 Gas Chromatograph equipped with a hydrogen-flame ionization detector.

The compounds shown in Figure 1, in order of emergence, are: 4-indanol-TMS ether, 5-indanol-TMS ether, 4- and 7-indenol-TMS ethers, and 5- and 6-indenol-TMS ethers. Previous work on a 20-foot by 1/8-inch packed column containing DC 550 silicone oil showed that the 4- and 7-indenol-TMS ethers could be separated, but not the 5- and 6-indenol-TMS ethers.

The conditions used to obtain the results shown in Figure 1 were: column temperature, 151° C; flash vaporizer temperature, 212° C; inlet pressure of N₂ carrier gas, 17.9 psi gauge.

In addition, larger samples were run on a column made from a piece of copper tubing, 610 cm. x 0.30 cm. I. D., coiled as a helix, and containing 12.4 grams of packing, made up in the weight ratio of 8 parts of D.C. 550 silicone oil to 92 parts of 60-80 mesh aqua regia washed Chromosorb. This was mounted in a Burrell K-3 Gas Chromatograph.

Figure 2 is a chromatogram of an indanol-indenol trimethylsilyl (TMS) ether mixture obtained by liquid-liquid chromatography run on this 20-foot silicone column. On the basis of relative retention-time measurements, peak A in Figure 1 is 4-indanol-TMS ether. Peaks B and C are believed to be the 4- and 7-indenol-TMS ethers.

Liquid-Liquid Chromatography of Indenols

The packings for the liquid chromatography experiments were made by absorbing an aqueous AgNO₃ solution onto dry Chromosorb. The AgNO₃ solution in a polyethylene squeeze bottle was sprayed in small increments onto the Chromosorb (in a flask), which was rotated and mixed between successive additions of the AgNO₃ solution.

The "wet" packing (which is still free-flowing) was then put into a glass column 69-inches long and of 3/4-inch inside diameter for the top 30 inches and 1/2-inch inside diameter for the bottom 39 inches. The glass column was jacketed to allow for passing cooling water or refrigerant around the chromatographic column.

The liquid-liquid chromatographic separation on an indanol-indenol mixture was made using a packing which contained 46.3 grams of AgNO₃ solution (60 grams AgNO₃/100 grams solution) per 110 grams of 80-100 mesh Chromosorb. This "wet" packing, 114.2 grams, was packed into the glass column described above. The sample of 0.60 gram of 4-indanol pyrolyzate (recrystallized from heptane) was dissolved in 40 milliliters of heptane, put onto the column, and eluted with 400 milliliters of heptane. During the run, the column was at room temperature. Selected 12-milliliter fractions (chosen on the basis of their refractive index) of the eluate were combined and evaporated to dryness (35° C maximum temperature). The phenolic residues were converted to their trimethylsilyl ethers, and analyzed by gas chromatography. The only substance eluted from the column was 4-indanol; the indenols were held on the column packing. After the heptane-eluted indanol had come out of the column, methyl isobutyl ketone (MIBK) was used and the indenol was then eluted in the MIBK-containing fractions.

The solvent from the indenol-containing fractions was evaporated off, and the trimethylsilyl ethers prepared from this phenolic mixture. This preparation contained a fine blackish precipitate, which suggests that the indenol was eluted from the column as a silver complex or salt, which was then decomposed during the preparation of the trimethylsilyl ethers, depositing metallic silver.

Preparation of Ion Exchange Column Containing Ag⁺

A chromatographic column was filled with 200 grams of 50-100 mesh Dowex 50-X8 cation exchange resin. An aqueous silver nitrate solution containing 95 grams of silver nitrate was poured through the resin filled column. The resin was washed with water and then air-dried. The silver impregnated resin was packed into the chromatographic column.

Separation of 5-Indanol and 5(6)-Indenol

A mixture containing 2 grams of 5-indanol and 5(6)-indenol was dissolved in a minimum amount of acetone and poured into the prepared column which had been wet with 60-68° petroleum ether. Elution was carried out with petroleum ether. Gas chromatographic examination of the eluate showed that only 5-indanol was present. Elution with chloroform removed the 5(6)-indenol, along with a small quantity of 5-indanol.

When larger amounts of indenol were put on the column, some indenol eluted with the indanol fraction. Elution with chloroform then gave pure indenol.

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The Design and Operation of Fluidized-Catalyst
Phthalic Anhydride Plants.

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The catalytic oxidation of naphthalene to phthalic anhydride by atmospheric oxygen is a reaction admirably suited for a fluidized reactor. Early attempts to produce phthalic anhydride on a commercial scale by this means ran into serious difficulties. This was because of mistakes in design and a lack of appreciation of many of the factors involved. It is proposed in this paper to describe how these difficulties have been overcome and also to indicate the essential features in design and operation for the trouble-free manufacture of phthalic anhydride by this method.

Fluidized-bed v. Fixed-bed.

Phthalic anhydride has been manufactured by the oxidation of naphthalene in fixed-bed reactors for more than forty years. During this time considerable design and operational experience has been accumulated. Nevertheless, it is widely known that such reactors have inherent defects which make impossible the desired control of reaction conditions. The advent of the fluidized-bed reactor has made possible not only a much closer approach to these ideal reaction conditions but also several other important advantages which favourably influence the economics of the process. Fig. 1. is a flow diagram of a fluidized-catalyst phthalic anhydride plant and below are listed some of the important advantages gained by this method of manufacture.

- (a) Greater Safety. The presence of finely divided catalyst in the reactor prevents explosions and so permits operation well inside the explosive range of air:naphthalene ratios.
- (b) More precise control of reaction conditions. The high thermal conductivity and good heat-exchange characteristics of this fluidized-catalyst bed permits an exact control of reaction temperature without the formation of hot spots. Temperatures varying only by one or two °F. can be held throughout a fluidized bed containing up to 30 tons of catalyst or more. Pressure, temperature, air:naphthalene ratio and contact time can each be varied, independently and quickly, so permitting a rapid and exact adjustment of operating conditions to meet particular requirements.
- (c) More efficient condensation of phthalic anhydride. A substantially lower air:naphthalene ratio makes possible the more efficient condensation of the reaction product because of its greater partial pressure in the product gases. Operating the reactor at increased pressure permits the condensation of 50% or more of the product directly as liquid, the balance being condensed as solid in switch condensers. The lower concentration of oxygen in the product gases, compared with that obtaining in fixed-bed plants, reduces the hazard of fire and explosion down stream from the reactor.

- (d) Liquid naphthalene feed. Fixed-bed phthalic anhydride reactors are fed with a mixture of air and naphthalene vapour involving the use of a separate evaporator. This can give trouble. With a fluidized-catalyst reactor liquid naphthalene is pumped directly into the reactor.
- (e) Catalyst charging. The tedious operation of charging catalyst pellets into the tubes of the fixed bed reactor is avoided. On the fluidized-bed plant catalyst can be moved pneumatically from the reactor to the catalyst storage vessel or in the opposite direction, even whilst the plant is operating.
- (f) Operation at increased pressure. The operation of fluidized-catalyst reactors at increased pressure (1 to 2 atm. gauge) permits a substantial increase in the output of a particular unit compared with its capacity at atmospheric pressure. Air compression cost must be balanced against higher throughput in order to determine the optimum operating pressure. The removal of the additional heat liberated as throughput is increased presents no serious design problems.
- (g) High purity product. The precise control of reaction conditions in a fluidized catalyst reactor results in the formation of a crude product of high purity. The redistillation process is thereby considerably simplified, and a final sales product of a high standard of purity is obtained. Table 1. gives the results of the analyses of a number of commercial samples of phthalic anhydride all taken independently and analysed blind. The higher quality of the samples from the fluidized-catalyst plants is apparent.

R. Landau and H. Harper (7) have given a critical, historical review of the development of phthalic anhydride technology. They mention the difficulties that have troubled the pioneers of the fluidized catalyst process. How these difficulties have been overcome is described below.

Condensation

The early fixed-bed phthalic anhydride plants were small and operated with high air:naphthalene ratios. The product was condensed in the so-called barns or hay boxes, which were large vessels, usually several in series. They served to slow down the gas velocity and wire net in the boxes provided additional surface for the condensation of the needle-shaped crystals of phthalic anhydride. The natural cooling of the boxes was usually sufficient for efficient condensation. With large production units, however, such barns are impracticable on the grounds of cost, danger and difficulties in handling the solid product. In modern plants they have been replaced by tubular heat exchangers operated as switch condensers. During condensation the tubes are cooled by water or oil at 35 to 40°C. Lower temperatures would promote the condensation of excessive amounts of water vapour with the concomitant formation of phthalic and maleic acids. For melting out, the cold water is replaced by high pressure steam and the cold oil by hot oil. A temperature high enough to dehydrate phthalic acid is essential otherwise it will accumulate inside the condenser reducing its efficiency and capacity and finally causing blockages.

Different types of tubular switch condensers have been described (3, 12); some are too complicated to be practicable in large production units. Besides simple heat-exchange considerations, other factors are involved in the design of efficient switch condensers. e.g., (1) Spare capacity is necessary to permit periodic cleaning of the tube bundles without interrupting production. (2) The capacity of the individual condensers must be such that the switch operation is relatively infrequent, otherwise there would be an excessive thermal load due to the relatively high heat capacity of the condensers which could be even more than the heat required to melt the phthalic anhydride. (3) The construction of the condensers should be such that

TABLE 1.

Source of Sample	Phthalic Anhydride %	Phthalic Acid %	Maleic Anhydride %	Naphtha-quinone %	Iron p.p.m.	Ash %	Crystallising Point °C	Colour Hazen Units	Colour after 2 hours at 250°C Hazen. Units
Fixed Bed A.	99.4	0.17	0.02	not detected	1.7	0.0006	130.6	45	113
Fixed Bed C.	99.1	0.65	0.17	"	2.0	0.0056	130.3	100	250
Fixed Bed E.	99.3	0.59	0.04	"	0.4	0.0010	130.3	90	225
Fluid Bed B.	99.6	0.08	0.01	"	0.4	0.0004	130.9	30	77
Fluid Bed D.	99.7	0.15	0.02	"	1.0	0.0028	130.8	65	97
Fluid Bed F.	99.3	0.40	0.01	"	1.9	0.0002	130.5	30	70
Fluid Bed G.	99.5	0.40	0.08	"	0.7	0.0004	130.7	25	60

the heat capacity is kept to a minimum. The oil system for cooling and melting is therefore preferred rather than the water/high pressure steam system. (4) The design should be such as to minimize or eliminate fire and explosion hazards. This can be achieved by the use of a closely packed gilled tube bundle. (5) It is not sufficient in condensers of this type merely to provide adequate cooling surface. Provision must also be made for ensuring that the product gases have the opportunity of contacting preformed phthalic anhydride crystal surfaces, otherwise even with more than adequate cooling, solid deposition will not necessarily occur. Fig. 2. shows a 6 ft. length of finned tube enclosed in glass pipe-line. The tube was cooled by passing water through it. Air saturated with phthalic anhydride vapour at 140°C was passed downwards through the annulus between the finned and the glass tubes. Solid phthalic anhydride was deposited on preformed crystals rather than on the cooler base portions of the finned tube. Vapour super-saturated with phthalic anhydride will leave the tube if the speed of the gas exceeds a low minimum value.

Fig. 3. shows diagrammatically a switch condenser which meets these requirements (14, 15). It consists of a relatively light gauge steel box packed with rows of vertical gilled tubes connected to manifolds. During the condensation part of the cycle, cold oil (40°C) is passed through these tubes. The product gases from the fluidized reactor enter the condenser and at first pass at relatively low velocity, more or less straight through the banks of gilled tubes. Massive, solid phthalic anhydride condenses on the first banks which become blocked and an increasing amount of the product gas passes through the gaps at the ends of the banks of gilled tubes. These gaps at opposite ends of adjacent rows prevent excessive build up of back pressure before a substantial quantity of phthalic anhydride is condensed. The increased gas velocity as the gas flows parallel to the rows improves heat exchange and gives good contacting of the product vapours with preformed phthalic anhydride crystals. As the product gases progress through the condenser the concentration of phthalic anhydride decreases and condensation occurs on the later banks of gilled tubes in the form of long needles. The close packing of the tubes no doubt also has a filtering action on any gas borne particles of phthalic anhydride.

At a predetermined time a condenser is taken off stream and the cold oil replaced by hot. The phthalic anhydride melts and is run to storage. The hot oil is then switched back to cold; after a period for cooling the empty condenser is again put on stream. It is essential to use a thermally stable oil for this purpose.

The United Coke and Chemical Company's plant operates on eight of these switch condensers together with a ninth stand-by for periodic special cleaning. At normal throughput a sequence of six condensing and two melting is employed. The capacity of the boxes is such that switching is carried out at long intervals and little or no advantage would be gained from automatic operation. Analyses have shown that a small amount of slip takes place at the commencement of the condensation i.e., when the tube surfaces are clean and cooling must be at its best, but when there is little or no solid phthalic anhydride to promote condensation. Long intervals between switching reduces the loss by slip to a very low value.

These condensers have been tested for long periods with air:naphthalene ratios as high as 30:1 and the results obtained indicate that they could be used advantageously with fixed-bed reactors.

Fluidized-catalyst reactors, operating with low air:naphthalene ratios and at increased pressure can advantageously condense an appreciable proportion of the product directly as liquid (2) and so decrease the thermal load on the switch condensers.

Filtration

In order to prevent contamination of the product and loss of an expensive catalyst it is essential in a fluidized-bed phthalic anhydride plant efficiently to filter the product gases. Early design proposals (4) suggested the use of cyclones. In the first production unit, the Sherwin Williams Company (6) developed the use of porous ceramic filters for the complete elimination of the catalyst dust at high temperature. Porous stainless steel filters have been used in pilot plants. The United Coke and Chemicals Company (13) have developed a fibre-glass filter. It consists essentially of a perforated steel cylinder (Fig. 4) having a spigot at each end. The upper spigot is threaded and serves to connect the filter to a collector box. The lower spigot is closed and serves to protect the filter. It also acts as a journal whilst the filter is being wrapped. The wrapping, which is done on a simple machine, consists of alternating layers of continuous-filament glass cloth and super-fine fibre-glass mat. The first 5 layers (3 cloth and 2 mat) are held in position by an open wound helix of glass tape. Another similar series of cloth, super-fine mat, cloth and tape, is added followed by an overlapping spiral wrap of glass tape and the whole bound firmly but not too tightly with jubilee or similar metal clips at 18" intervals. The overlapping ends of the glass cloth are secured in grooves at the two ends of the filter tube, by means of fibre-glass cord. This is an additional precaution to prevent end leakage. Four separate collector boxes are used, each carrying several of these fibre-glass filters. By means of a process controller each bank of filters can be blown back in turn to detach filter cake from the outer surface. More than ten years of operational experience has shown that these filters are a reliable means of obtaining 100% filtration of catalyst dust from the product gases at a temperature of about 300°C. They have advantages over porous ceramic filters in that they are not brittle, they can be quickly and relatively cheaply re-wrapped and if necessary, can be made to operate at low back pressure. On blow-back, the slight "give" in the fibre-glass wrapping tends to cause better removal of the accumulated filter cake. The back pressure across the filters depends, of course, on the surface area of the filter and the volume of gas passing. It is customary to operate fluidized-catalyst phthalic anhydride plants under pressure so a filter pressure drop of 4 to 6 lb. p.s.i. or more can be accommodated. Filter candles up to 12 ft. in length have been successfully used. Experiments have also been carried out in which these filters have been operated at 10 to 20 ins. w.g. back pressure for prolonged periods at 300°C.

The positioning of the filtration unit in the plant is important and is discussed below.

The Fluidized-bed Catalyst.

The physical and chemical nature of the catalyst is of great importance for the trouble-free operation of a large fluidized-bed phthalic anhydride plant. Not only must it have high and specific reactivity but also good fluidizing properties, high attrition resistance and long life. The catalysts used in the early days of this new technique were formulated on the grounds of their catalytic activity with little or no attention to their fluidizing properties and attrition resistance. It is possible in laboratory apparatus and small pilot plants to obtain reasonably good fluidization and excellent conversions of naphthalene into phthalic anhydride with a wide range of catalysts. Nevertheless, in full scale reactors troubles can arise from the use of friable catalysts with the consequent rapid accumulation of an excessive proportion of fines in the fluidized bed. This may bring about uneven fluidization and an undesirably high concentration of fines in the expanded phase. Both these states can give rise to trouble; the latter is probably a contributory cause to "after burning" (see below), whilst the former may bring about the formation of static pockets of catalyst. Such pockets in contact with the reactor walls can act as naphthalene condensers. The mixture of solid naphthalene and catalyst so

formed, if suddenly disturbed and ignited can react very vigorously with the production of excessively high temperatures within the fluidized bed.

Fluidized-bed phthalic anhydride catalysts must have a fairly high specific surface and a relatively large pore diameter. These properties are not compatible with high attrition resistance so it is necessary to compromise. It has been found possible to formulate a highly specific catalyst with the required attrition resistance and long life. In a favourably designed reactor, size degradation is surprisingly slow and present indications are that it should be possible to maintain the activity and good fluidizing properties of the catalyst with a replacement level as low as 10% per annum.

After Burning

One of the most serious and dangerous difficulties which beset pioneers in this field was "after burning", i.e. the ignition of the product vapours above the fluidized-catalyst bed with a consequent excessive and sometimes disastrous rise in temperature. This has already been described in some detail (1). In the absence of effective temperature control in the expanded phase, temperatures as high as 750 to 1000°C or more may be reached with consequent serious damage to the filters, catalyst and reactor. The most likely explanation of this phenomenon is excessive slip of naphthalene through the fluidized catalyst dense phase occasioned by poor fluidization, particularly slugging, spouting, rat-holing or an excessive proportion of bubble phase in the boiling bed. A small amount of particularly active, static catalyst lodged somewhere above the fluidized-bed possibly starts the exothermic oxidation of this naphthalene. (11) and with a relatively rapid rise of temperature initiates the after burning. Whatever the cause, after burning can be prevented by keeping the temperature of the expanded phase well below that of the bed. Various methods of doing this can be used:-

- (1) Cooling tubes in the expanded phase. Although the heat-exchange coefficient on the gas side of the tubes is not favourable, the dust concentration in the gas increases the amount of cooling over that which would obtain with a clean gas.
- (2) Quench Zone. A specially cooled extension of the fluidized bed to cool the gases leaving the reaction zone has been described by the American Cyanamid Company (1). It necessitates the use of an additional distributor plate, special cooling coils and a standpipe. This upper part of the fluidized bed is termed the "quench zone" and it is recommended that the temperature of this zone is kept at least 50°C below that of the main fluidized bed. Such an arrangement could, if not properly designed and operated, lead to an increased rate of catalyst attrition (see below).
- (3) Quench Gas. The temperature above the bed can be effectively controlled by the introduction of cold air, or better, cold inert gas. This simple and practicable method has the advantage of reducing the concentration of phthalic anhydride in the product gases, which, of course, is not good from the condensation angle.
- (4) Recycling cooled catalyst. Recycling cooled catalyst through the expanded phase can be used to cool the gases leaving the boiling bed. This, however, may result in increasing catalyst attrition to an objectionable rate.
- (5) External cooling. If the catalyst filters are housed in separate vessels, then it is possible to cool the product gases by utilizing the surface of the interconnecting pipe-lines. This is effective in preventing after burning but involves catalyst circulation at high velocity, which may contribute to catalyst attrition (see below).

Another factor which makes an important contribution to minimising the risk of after burning is low oxygen partial pressure in the product gases. This is achieved by operating at the lowest possible air:naphthalene ratio compatible with crude product purity and bed temperature.

Trouble from after burning has been virtually eliminated from modern fluidized-catalyst phthalic anhydride plants by the use of one or more of the above devices.

Reactor Design and Catalyst Attrition

There is an upper limit to the attrition resistance which can be built into an acceptable naphthalene oxidation catalyst. Reactor design should therefore be such as to keep catalyst attrition to a minimum; otherwise excessive catalyst replacement will be necessary in order to prevent a built up of an excessive proportion of catalyst fines. This also places a limit on the fluidizing gas velocity and emphasises the important advantage of operating fluidized-catalyst reactors at increased pressure in order to obtain the necessary contact time and economic throughput. Three design features are involved in minimising catalyst attrition viz., (1) the disposition of the catalyst cooler, (2) the disposition of the filters and (3) the distributor plate. These are discussed below.

- (1) The Catalyst Cooler. Some of the earlier patents (16) describe fluidized catalyst reactors having external heat exchangers. These require the pneumatic conveying of catalyst at high velocity through transfer pipes and the narrow tubes of the heat exchangers. The action of the frictional and impact forces involved on the catalyst particles, particularly so when sudden changes in direction are involved, must increase the rate of attrition. The consequent more rapid build up in the concentration of catalyst fines not only gives rise to the difficulties mentioned above but must also decrease the efficiency of the cooling system. R. M. Braca and A. A. Fried (5) have described the attrition which occurred in a fluidized-catalyst phthalic anhydride plant. No catalyst make up was used and after two years operation the proportion of catalyst particles less than 20 μ had increased from 9 to 48 per cent. This fine material plated out on the tubes of the catalyst cooler and about half of them gradually became blocked. The installation of cooling tubes within the fluidized-catalyst bed overcomes this drawback. The excellent thermal conductivity of the fluidized catalyst and the good heat-exchange characteristics of the system make this possible.
- (2) The Filters. Commercial phthalic anhydride plants differ in the disposition of the catalyst filters. Some of them house the filters in a number of separate vessels, each connected to the top of the reactor by a pipe-line. The catalyst fines which accumulate on the surface of the filters are periodically blown off and conveyed back into the base of the fluidized-bed by means of some of the fluidizing air. The attrition to the catalyst fines thereby caused will, of course, be much less than that which would obtain if coarser particles were involved. Nevertheless, it will make some contribution to the rate of catalyst attrition.

Other phthalic anhydride plants have the filter units located in the top of the reactor itself. On blow-back, the catalyst filter cake falls back into the reactor and the transfer of catalyst at high velocity through pipe-lines is thus avoided. This simple arrangement of filters, however, makes somewhat more difficult the problem of cooling the product gases issuing from the boiling catalyst bed. An increase in the height of the knock-out zone above the fluidized bed overcomes this difficulty.

- (3) The Distributor Plate. In the fluidized-catalyst reactor it is important to establish reasonably uniform distribution of air and naphthalene vapour across the whole bed, otherwise the air:naphthalene ratio would vary from place to place and hinder the attainment of optimum reaction conditions. The height:diameter ratio of the fluidized-catalyst bed and the low density of the catalyst are both favourable to good fluidization. Nevertheless, in a large fluidized reactor, say 10 ft. diameter or more, it is essential to operate with an appreciable pressure drop across the distributor plate, otherwise there is a danger of uneven air distribution. Various methods of attaining even distribution have been proposed. e.g., (a) the use of multi-jets instead of holes (9); (b) the gas is introduced through a flared, conical-shaped zone at the base of the reactor, high turbulence being maintained in this zone and a distributor plate is not used (8). Another proposal (17) is to subject the reactor, which has a conical bottom, to vertical linear oscillations, 100 per sec., with an amplitude of 1.5 mm. These methods would lead to additional catalyst attrition, particularly the one using high velocity jets. T.J.P. Pearce and I.C.I. Ltd., (10) have suggested the use of a suitable porous ceramic plate. Its maintenance in a large reactor would possibly be difficult. A method of obtaining any desired pressure drop across a distributor plate without high velocity air streams increasing catalyst attrition would be by use of the device shown in Fig. 5. Instead of a simple hole the small conical filter elements are inserted in the distributor plate. The entry holes to the filters could be made small enough to give back pressure necessary for good distribution. The air used for fluidization would have to be filtered to prevent the slow clogging of the small filters from the underside.

It is not difficult in a laboratory fluidized reactor, or in a pilot plant reactor to obtain relatively uniform fluidization and consequently a high degree of control of reaction conditions. This is evidenced by the results given in Table 2.

TABLE 2.

Results obtained in a 2 in. diam. laboratory fluidized-catalyst reactor using pure naphthalene (0.07% S).

Temp. °C	Air:Naphthalene Ratio	Yields % w/w.		
		P.A.	M.A.	N.Q.
350	15:4	104.5	1.7	0.7
330	11:5	104.1	1.1	0.9
320	14:0	104.2	1.5	1.2

Pilot plant results obtained in a 6" diam. fluidized-catalyst reactor using petroleum naphthalene (S free) c.p. 79.4°C.

Temp. °C	Air:Naphthalene Ratio	Crude Yield %	Analysis of Crude %		
			P.A.	M.A.	N.Q.
335	15:1	100.2	98.0	0.09	1.6
340	15:1	99.7	98.5	0.13	0.7
350	15:1	99.8	97.9	0.19	1.1

It is possible that the quality of fluidization and distribution in a full scale plant can be assessed by their approach to laboratory results.

Sulphur in Naphthalene

The principal impurity in phthalic grade, coal tar naphthalene is thionaphthene which boils only 4°C above the b.p. of naphthalene. Naphthalene derived from tar from sulphurous coals may contain 1% sulphur, which is equivalent to 4.19% thionaphthene. Catalysts which have been used in the past in fluidized-bed reactors have tended to deactivate when sulphurous naphthalene is used as the feed (6). It has been stated that sulphur-free naphthalene (sodium treated) is required for optimum conversion to phthalic anhydride. This is no longer so as a sulphur-resistant fluidized-bed catalyst is now available. It has also been claimed (18) that the presence of sulphur in the naphthalene is advantageous in preventing catalyst deactivation. The oxidation of thionaphthene, however, cannot yield phthalic anhydride, so its presence in naphthalene must mean an equivalent loss of phthalic anhydride yield.

In order to determine whether or not excessive amounts of thionaphthene had any deactivating action on the new fluidized-bed catalyst the following work was carried out. Naphthalenes were prepared containing increasing proportions of thionaphthene (0 to 4.75% S) as the principal impurity. These were oxidized with air in a laboratory fluidized catalyst apparatus. The results obtained are shown in Fig. 6. There is a proportionate falling off in the phthalic anhydride yield as the thionaphthene content of the naphthalene feed increases and there is also a steady increase in the maleic anhydride yield. A final oxidation using again a sulphur-free naphthalene feed gave results quite close to those obtained initially, indicating that the excessive proportion of sulphur had not deactivated the catalyst. A sulphur free naphthalene gives a proportionately higher yield and probably also, less corrosion in the condensation system. The lower maleic anhydride content of the crude product will probably reduce distillation losses during the final purification. Whether or not pure or sulphurous naphthalene should be used as feed for a fluidized phthalic anhydride plant is a question to be answered by the economics of the operations.

Pilot plant experiments in a 6" diam. fluidized catalyst reactor were carried out using two different coke-oven naphthalenes (a) c.p. 77.6°C ; S, 0.87% and (b) c.p. 79.6°C ; S, 0.31% and Ashland petroleum naphthalene c.p. 79.4°C ; S, 0.00%. A range of operating conditions was used for each naphthalene. Table 3 gives the yields obtained under the optimum operating conditions. These results indicate that the presence of thionaphthene in the naphthalene feed does not wholly account for the reduction in yield.

TABLE 3.

<u>Naphthalene</u>	<u>Reaction Temp. $^{\circ}\text{C}$</u>	<u>Average Yield of Crude %</u>	<u>Analysis of Product %</u>		
			<u>P.A.</u>	<u>M.A.</u>	<u>N.Q.</u>
Coke Oven 0.87% S	350	91.3	97.5	0.56	0.6
Coke Oven 0.31% S	340	96.1	98.5	0.18	trace
Petroleum 0.00% S	335	100.2	97.9	0.19	1.1

Conclusion

Apart from the catalytic cracking of petroleum, the development of the fluidized-catalyst technique in the chemical manufacturing industries has been relatively slow. This has been largely due to the state of our fundamental knowledge of the properties of fluidized beds and of heterogeneous catalysis in such beds.

The methods adopted for overcoming the difficulties in developing the fluidized-bed method for naphthalene oxidation described above are already being successfully applied to other processes, particularly to exothermic oxidations. There is little doubt that the success achieved with the phthalic anhydride process will accelerate the wider industrial use of fluidized-bed catalysis.

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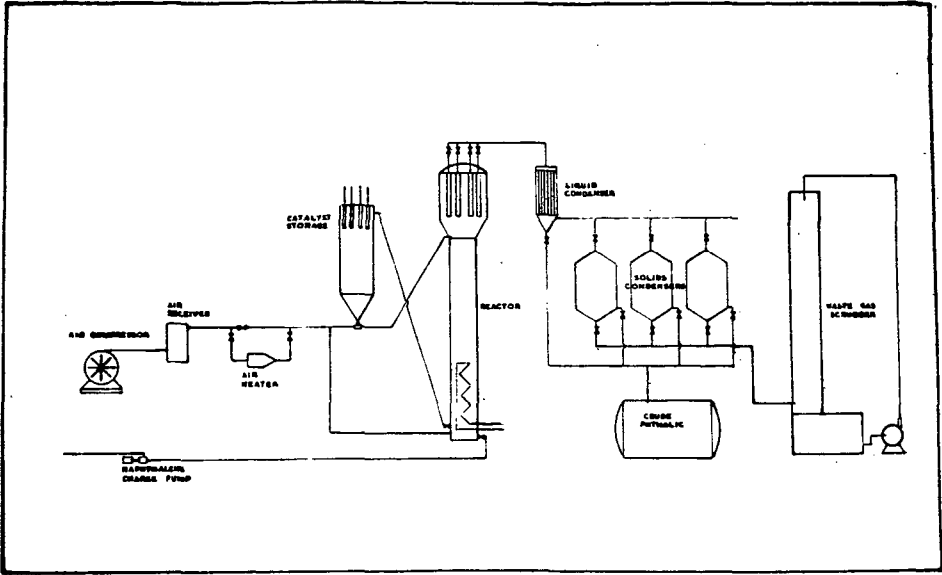


Fig. 1. Fluidized Catalyst Phthalic Anhydride Plant.



Fig. 2. Condensation of phthalic anhydride on cooled finned tube.

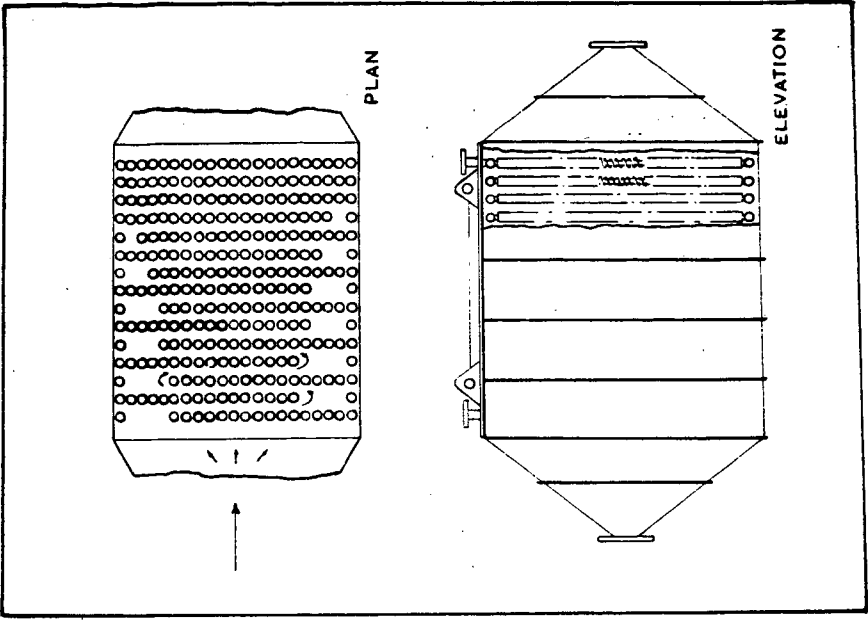


Fig. 3. Switch Condenser.

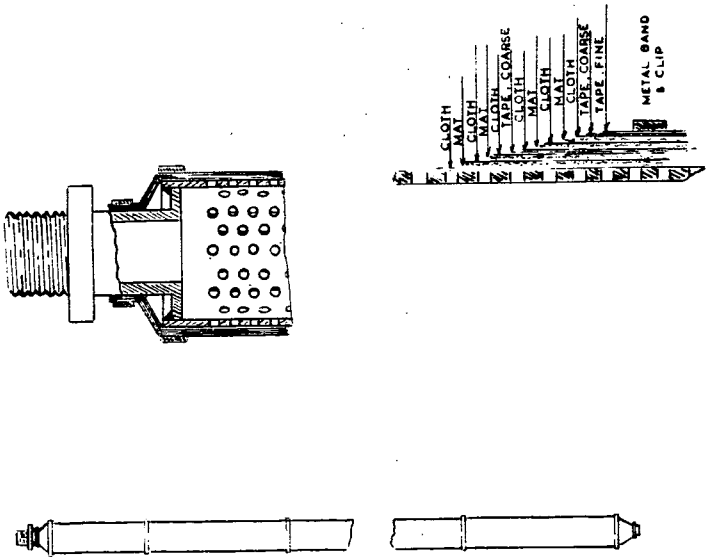


Fig. 4. Fibre-glass Filter.

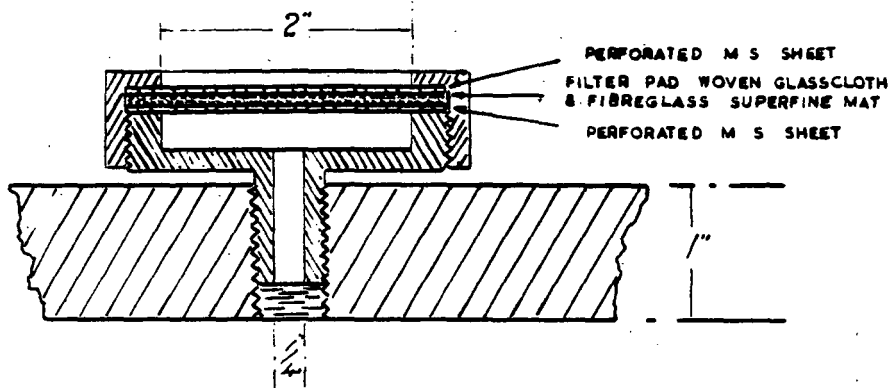
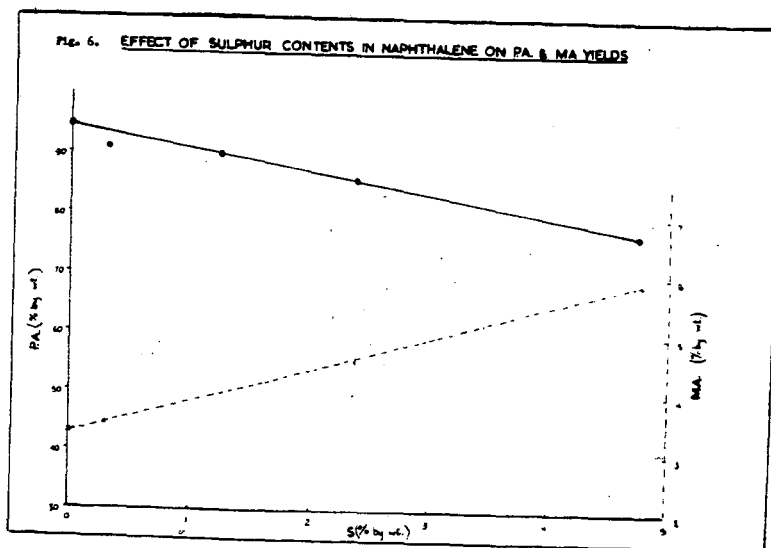


Fig. 5. Distributor Plate Filter.



Antioxidants from Tar Acids

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Before delving into the subject at hand, namely the manufacture of antioxidants from tar acids, it would be wise for us to define our terms and the scope of this discussion. By tar acids we mean the "acidic" or base-soluble fraction of coal tar. These same tar acids are also available from petroleum sources. Furthermore, both phenol, parent compound of the tar acids, and p-cresol are made synthetically. While phenol is the major constituent of tar acids, the synthetic material accounts for over 90% of the market. Its precursors, benzene or toluene, are also coal chemicals which are again mostly derived from petroleum sources. Benzene is also the starting material for styrene, an important chemical intermediate in the antioxidant field. As far as the end products are concerned, we shall limit our discussion to the phenolic antioxidants, realizing at the same time that there are non-phenolic antioxidants prepared from tar acids as there are phenolic antioxidants not prepared from tar acids. It is apparent that the coal tar industry does not enjoy an exclusive position as supplier of raw materials for the manufacture of phenolic antioxidants.

Despite the fact that the coal tar industry was at one time the only producer of tar acids, the early work on phenolic antioxidants was not done by this industry. Rather, those industries manufacturing items subject to oxidative degradation saw a need to stabilize their products and therefore investigated the use of antioxidants. Such industries include gasoline, food and animal feed, rubber and plastics, lubricating and transformer oils. As a result, most of the research, both that dealing with the theoretical aspects of oxidation and inhibition, and that dealing with the development of new and better antioxidants, was carried out by the potential users of antioxidants. Even the manufacture of antioxidants has been almost exclusively in the hands of the users and a few chemical manufacturers.

The application of phenolic antioxidants in the various fields was based on the finding by Moureu and his co-workers (1) that acrolein could be stabilized by the addition of certain phenols in small amounts. The use of stabilizers such as tannin and hydroquinone in rubber was described by Helbronner and Bernstein (2). At the 71st meeting of the American Chemical Society at Tulsa, in April of 1926, Smith and Wood (3) presented a paper entitled "Inhibiting Agents in the Oxidation of Unsaturated Organic Compounds" dealing with the oxidation inhibition in soaps, fats and oils. In the gasoline field, an initial emphasis on color stabilization gave way to gum prevention by inhibitors (4,5).

Closer scrutiny of the type of substances used in these and other applications led to theories on the mechanism of the oxidative degradation, its inhibition, and subsequently, to a more systematic study of the types of compounds which may be used advantageously to perform this function.

Here are several recent references which may serve as a starting point for those who wish to pursue this phase further.

Lundberg⁽⁸⁾ recently edited a monograph entitled "Antioxidation and Antioxidants." Ingold⁽⁷⁾ also reviewed the literature in 1961. A recent paper presented before the Division of Petroleum Chemistry at the last ACS meeting at Atlantic City was that by Hedenburg⁽⁹⁾ of the Gulf Research Laboratories.

In the studies performed to find a correlation between the structure of an antioxidant and its activity, whole groups of substituted phenols were prepared and tested⁽⁹⁻¹⁵⁾ as antioxidants. This led to the finding that sterically hindered phenols, i.e. phenols in which the hydroxyl group is sterically hindered, gave the desired properties. In general, it was found that the more hindered the phenol was, the better was its antioxidant activity. However, only last year it was found by Spacht and his co-workers at Goodyear⁽¹⁶⁾ that too much steric hindrance had a deleterious effect on antioxidant activity.

Let us consider the commercial phenolic antioxidants and the modes of their manufacture. Of primary interest is 2,6-di-t-butyl-p-cresol (I). Some 17 million pounds of this compound was produced in 1961. Even at that, it may not be the phenolic antioxidant made in greatest quantity, but it has been used most widely including all the applications mentioned earlier. It is known in the food industry as BHT (which stands for butylated hydroxy toluene) and the various manufacturers have their own trade name for it.

When we look at the structure we immediately realize that it is the reaction product of p-cresol and a source of t-butyl groups, such as isobutylene, t-butyl chloride or t-butyl alcohol. Of these, the olefin is preferred for ease of operation and for reasons of economics. While synthetic p-cresol is available and is the source of most of the BHT produced, those active in the coal tar field will have realized immediately another source of p-cresol, namely the tar acids. There is one difficulty, however - p-cresol occurs along with its more abundant isomer, m-cresol, from which it cannot be separated by fractional distillation; the two isomers boil within one degree of each other. Various physical means of separation have been investigated but it turns out that conversion to the desired compound, BHT, is one of the simplest means of separating meta- and para-cresol^(17,18,19). This is made possible again by a phenomenon which was mentioned before, namely steric hindrance. When a mixture of meta- and para-cresol is alkylated with isobutylene, the initial products are mono t-butyl derivatives. In the case of p-cresol (II), the t-butyl group enters the position ortho to the hydroxyl group as expected by the stronger ortho-para directing influence of the hydroxyl group over that of the methyl group. Since both ortho-positions are identical, only one compound will be formed. This compound is 2-t-butyl-p-cresol (III). In the case of m-cresol (IV), there are three choices, two dissimilar ortho positions as well as an open para position. However, steric hindrance prevents the introduction of the t-butyl group in the ortho position between the hydroxyl and the methyl groups. As a matter of fact, steric hindrance between a methyl and an adjacent t-butyl group makes the normally more stable position para to the hydroxyl group thermodynamically less stable so that the t-butyl group positions itself ortho to the hydroxyl and para to the methyl group to give us 6-t-butyl-m-cresol (V). Unfortunately, the compound described in the literature for many years^(18,20,21,22) as 4-t-butyl-m-cresol was actually 6-t-butyl-m-cresol⁽²³⁻²⁶⁾. The real 4-t-butyl-m-cresol was not made until about 1948^(27,28,29). The two ortho-t-butylated cresols which are thus obtained as the first reaction products from the treatment of m,p-cresol with isobutylene, are also inseparable by fractional distillation.

Further alkylation produces the dibutyl derivatives; on the one hand, the desired compound, 2,6-di-t-butyl-p-cresol, and, as the m-cresol derivative, the para alkylated 4,6-di-t-butyl-m-cresol (VI). These two compounds, the first, an ortho-ortho dibutylated cresol and the latter, an ortho-para dibutylated cresol have boiling points sufficiently far apart for easy separation by fractional distillation. The

distilled BHT can be further purified by washing and crystallization. When p-cresol is made synthetically, it is not admixed with its meta isomer. The alkylation of pure p-cresol is the same as that described for the mixed isomers.

No mention was made of any conditions for the alkylation nor was the catalyst identified. The reason for these apparent omissions is that a variety of alkylation catalysts, such as sulfuric acid, sulfonic acids, phosphoric acid, boron fluoride and solid catalysts, is possible even if we restrict ourselves to isobutylene as the alkylating agent. Furthermore, each catalyst may be used in various concentrations. These factors permit great latitude in the choice of the other reaction conditions such as time and temperature.

A second antioxidant, which has been known for its activity, but which is not widely used in the U.S., is 6-t-butyl-2,4-xyleneol (VII). I specified the American market, because it is a commercial product of long standing in Great Britain.

Looking at its structure, one will immediately realize its close structural relationship to BHT. The difference between the two compounds is the replacement of one of the o-t-butyl groups in BHT by a methyl group.

As in the case with m,p-cresol, one of the precursors for 6-t-butyl-2,4-xyleneol, namely 2,4-xyleneol (VIII), occurs, in tar acid along with its isomer, 2,5-xyleneol (IX). The ratio of the two is roughly 2:1 in favor of the 2,4-isomer. While other xylenols are separable from the desired isomer by distillation, the above two isomers boil within one degree of each other.

Again, one can resort to t-butylation not only as a means of obtaining our desired antioxidant but also as a means of separating the two xyleneol isomers. The same principles which have been discussed in the m,p-cresol alkylation apply in the present case. As a matter of fact, the mixture of 2,4- and 2,5-xyleneol may be viewed as a mixture of ortho-alkylated m,p-cresols, the 2,4-xyleneol being the ortho-substituted p-cresol, and the 2,5-xyleneol, the ortho-substituted m-cresol. This makes them comparable to the mono-butyl m,p-cresol, each of which can only be t-butylation further with one group. In the one case, the second group entered the free ortho position to give BHT, and in the second, the para position. In the xylenols, one also finds that 2,4-xyleneol t-alkylates in the accessible 6-position to give the desired compound, 6-t-butyl-2,4-xyleneol while in the case of 2,5-xyleneol, the 4-position is alkylated to give 4-t-butyl-2,5-xyleneol (X) (19).

The isolation of the desired compound may be accomplished in various ways. One means, which is also applicable to the di-t-alkylation of m,p-cresol, takes advantage of the difference in the reactivity of the two isomers. Therefore, by using a limited amount of the olefin, choosing reaction conditions mild enough to enhance the selectivity, and limiting the reaction time to suppress or at least reduce equilibration, it is possible to alkylate 2,4-xyleneol in preference to the 2,5-isomer (30).

The unreacted xylenols, now predominantly the 2,5-isomer, are removed by distillation from the 6-t-butyl-2,5-xyleneol.

Another method of isolating 6-t-butyl-2,4-xyleneol made from 2,4-2,5-xyleneol is to carry the reaction further than in the previous example so that 4-t-butyl-2,5-xyleneol is formed in appreciable amounts. The reaction mixture is then added to dilute caustic which dissolves only the non-hindered phenols, namely any unreacted xylenols and the 4-t-butyl-2,5-xyleneol, but does not react with the hindered 6-t-butyl-2,4-xyleneol. Steam distillation of the mixture then carried over this product (31).

Work carried out during recent years has led to selective ortho alkylation of phenols with open para positions. Based on selective ortho alkylation⁽³²⁾ Neuwirth and his co-workers⁽³³⁾ have devised another route to 6-t-butyl-2,4-xyleneol, starting with o-cresol (XI). t-Butylation under these conditions gives 6-t-butyl-o-cresol (XII) and a Mannich reaction on this with formaldehyde and dimethylamine yields 4-dimethylaminomethyl-6-t-butyl-o-cresol (XIII). This is then treated with hydrogen, to give 6-t-butyl-2,4-xyleneol and dimethylamine as the products of the hydrogenolysis. The amine is then recycled to the Mannich reaction.

The work by Kolka, Ecke and their co-workers in this country^(34,35) and by Stroh in Germany^(36,37) has led to an economical synthesis of 2,6-di-t-butyl-phenol (XIV) which had been known for some time^(38,39). This compound is presently marketed by Ethyl and it serves as starting material for a number of derivatives which are antioxidants in their own rights.

Besides the t-alkyl derivatives, specifically t-butyl derivatives, of tar acids, the α -methylbenzyl or styryl derivatives of the phenols are of great commercial importance as antioxidants. Specifically, styrenated phenol itself (XV) is probably the alkylated tar acid made in greatest amount for use as antioxidant. This material, however, is not a pure compound, and not even a mixture of positional isomers. Rather, it is the reaction product of the styrenation of phenol, and, therefore, could contain, along with mono-, di- and tri-styryl phenols, phenol substituted with low molecular weight polymers of styrene such as dimers and trimers. These would be the results of a preliminary polymerization of styrene followed by alkylation of phenol with the resultant oligomers. It is obvious that a complex mixture is possible. So-called "alkylated styrenated phenols" are also commercial products. While styrenation may be considered a special form of alkylation, the designation "alkylated styrenated," probably denotes the fact that these products contain both styryl and t-alkyl side chains on phenolic nuclei.

A second major group of phenolic antioxidants include those produced from phenols, especially sterically hindered ones such as t-alkylated phenols, via subsequent reactions. The most important subdivision of these is the group in which two or more phenolic nuclei have been linked together. The bridging of these nuclei may consist of a number of groups, predominantly alkylidene, such as methylidene, or thio groups. On the other hand, the phenolic nuclei may be directly linked to each other. While two routes present themselves for the preparation of these compounds, namely alkylation of the tar acids followed by coupling, and the reverse order, it is the first which is usually practiced to give industrially important antioxidants. Usually, only two phenolic groups are linked. The advantage of these higher molecular weight materials is low volatility, a desirable property both during the processing of polymers in which they find major use, and during the remainder of the life of the articles made from the polymers.

If pure p-cresol rather than a mixture of m- and p-cresol is alkylated with isobutylene, the monobutyl-p-cresol (III) can be readily separated by distillation from the other materials in the reaction mixture. These would be the unreacted p-cresol and BHT. The 2-t-butyl-p-cresol is then reacted with formaldehyde under acidic conditions to give 2,2'-methylenebis (4-methyl-6-t-butylphenol) (XVI)⁽⁴⁰⁾.

In a similar fashion, 2-t-butyl-4-ethylphenol can be prepared from 4-ethylphenol and then converted to its methylenebis derivative.

In the m-cresol series, the most important alkylidene derivative is 4,4'-butylidenebis (2-t-butyl-p-methylphenol) (XVII) obtained as the product from the condensation of 6-t-butyl-m-cresol (V) and butyraldehyde⁽⁴¹⁾. However, since the only source of m-cresol is that admixed with its isomer, p-cresol, and since the two monobutyl derivatives of these could not be separated by distillation, the only

possible source of 6-t-butyl-m-cresol is the dibutyl-m-cresol (VI), which we obtained along with 2,6-di-t-butyl-p-cresol. Partial dealkylation of 4,6-di-t-butyl-m-cresol gives a mixture high in the desired 6-t-butyl-m-cresol along with m-cresol (IV) and unreacted starting material. The dealkylations in the presence of various catalysts take place under more severe temperature conditions than do the reverse alkylations. Two other bisphenols namely 4,4'-methylenebis (2,6-di-t-butylphenol) (XVIII) and 4,4'-methylene (6-t-butyl-o-cresol) (XIX) are now commercial products as a result of selective ortho alkylation. The latter is, of course, a derivative of o-cresol. The preparation of these bisphenols is carried out under basic conditions (42,43,44).

Trisphenols have also been made. However, only one (XX) derived from p-cresol, 2-t-butyl-p-cresol and formaldehyde, seems to be of commercial importance. The preparation of trisphenols is more complex than that of bisphenols. In the latter case only one compound is possible. In the preparation of trisphenols, a number of products are possible, and therefore, the reaction is carried out stepwise (45).

Almost all of the alkylidenebis compounds have thiobis counterparts, i.e. compounds in which the two phenol rings are coupled by a sulfur linkage. This coupling is accomplished by the reaction of the mononuclear phenolic compound with sulfur dichloride. Catalysts have been used in this reaction (46) but are not necessary. Of greatest importance is 4,4'-thiobis (6-t-butyl-m-cresol (XXI) (47). Others are the thiobis derivatives of 2-t-butyl-p-cresol (XXII) and 6-t-butyl-q-cresol (XXIII).

Several other phenolic antioxidants derived from tar acids have recently been introduced. All are the products of the reactions of ortho alkylated phenols. Starting with 2,6-di-t-butylphenol (XIV), oxidative coupling and reduction yields 4,4'-bisis (2,6-di-t-butylphenol) (XXIV) (48). This is a biphenol in which the two phenolic rings are linked directly to each other. Two other antioxidants based on 2,6-di-t-butylphenol are the p-methoxymethyl and the p-dimethylaminomethyl derivatives. The former (XXV) is the product of the reaction of the phenol, formaldehyde and methanol (43,48,49,50). The amino (XXVI) compound results when the phenol, formaldehyde and dimethylamine are reacted in a Mannich reaction (48,51).

In summary, alkylation, especially t-butylation and styrenation of tar acids to give sterically hindered phenols is the most important chemical reaction for the preparation of antioxidants. Secondly, the joining together of two or more phenolic nuclei with each other via a phenol-aldehyde condensation, a phenol-sulfur dichloride condensation, or an oxidative coupling is of major importance. To a much lesser degree, the reaction of a phenol, an aldehyde and a third compound with a replaceably hydrogen leads to antioxidants.

When the major antioxidants are broken down according to the starting tar acids, it becomes apparent that phenol, o-cresol, m,p-cresol and 2,4-2,5-xyleneol are the acids used to make the phenolic antioxidants. Phenol yields styrenated phenols, 2,6-di-t-butylphenol and its derivatives. o-Cresol yields the o-t-butyl derivative which is then converted to the methylenebis and the thiobis compound. p-Cresol is alkylated to 2-t-butyl-p-cresol as an intermediate for the manufacture of its methylenebis and thiobis derivatives, and to BHT. The monobutyl-p-cresol and the parent p-cresol are also reacted with formaldehyde to give 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-p-cresol, a trisphenol. m-Cresol is converted to its monobutyl derivative, 6-t-butyl-m-cresol, via the dibutyl derivative. The monobutyl cresol is then converted to its 4,4'-butylidenebis and its thiobis derivatives. Finally, a mixture of 2,4- and 2,5-xyleneol is butylated and the 6-t-butyl-2,4-xyleneol is isolated.

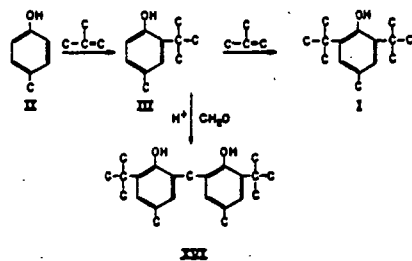
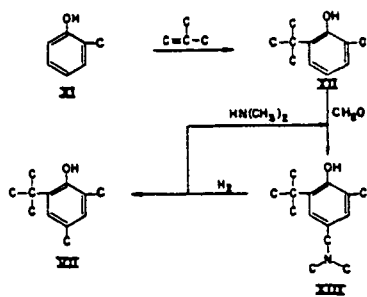
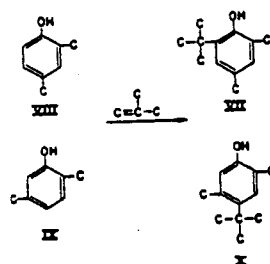
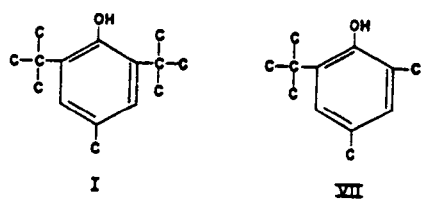
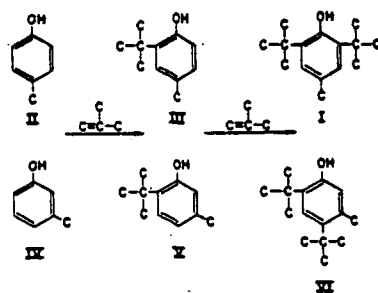
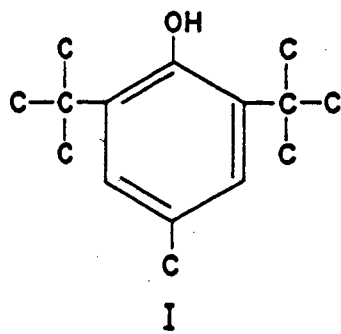
While this is a survey of tar acid-derived phenolic antioxidants, it must be remembered that there are other phenolic antioxidants, not derived from tar acids (just as there are non-phenolic antioxidants derived from tar acids). Even within the realm presented here, hundreds of structures have been prepared for antioxidant evaluation. Some of these are good antioxidants but have not been brought to commercialization for one reason or another.

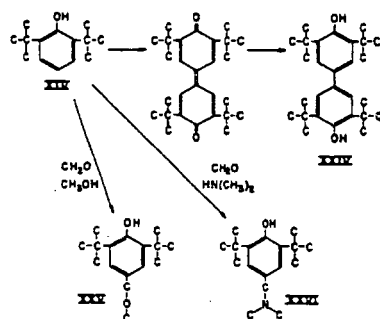
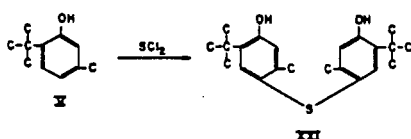
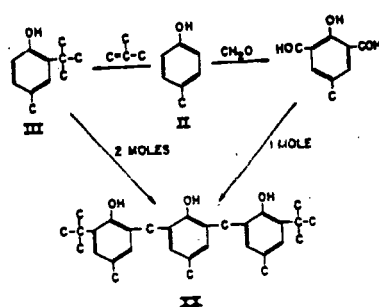
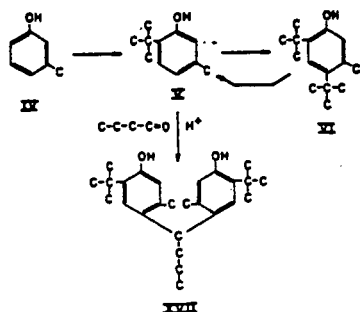
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1) TAR ACID + OLEFIN $\xrightarrow{H^+}$ STERICALLY HINDERED PHENOLS.

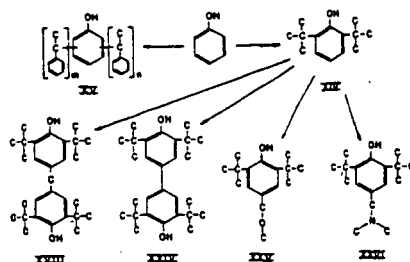
2) a. ALKYLATED PHENOLS + ALDEHYDE $\xrightarrow{H^+}$ ALKYLIDENE BIS PHENOLS

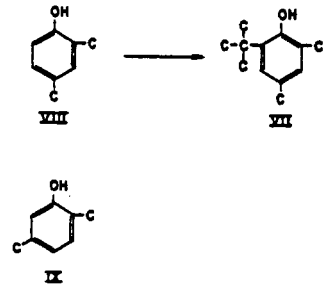
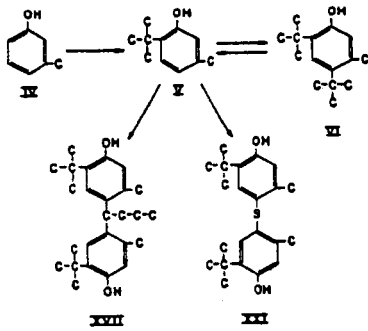
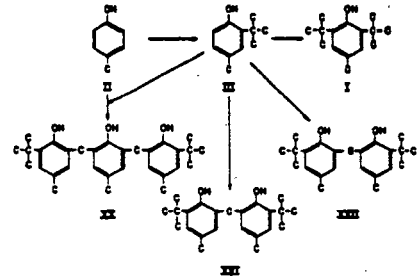
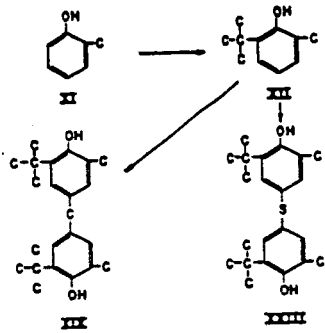
b. ALKYLATED PHENOLS + SULFUR DICHLORIDE $\xrightarrow{H^+}$ THIOPHENOLS

c. ALKYLATED PHENOLS $\xrightarrow{\text{OXIDATIVE COUPLING}}$ ALKYLATED BIPHENOLS

3) a. ALKYLATED PHENOLS + ALDEHYDE + AMINE \longrightarrow AMINOMETHYLPHENOLS

b. ALKYLATED PHENOLS + ALDEHYDE + ALCOHOL \longrightarrow ALKOXYMETHYLPHENOLS





Solvent Extraction of Tar Acids From Various Sources

D. C. Jones and M. B. Neuworth

Consolidation Coal Company
Research and Development Division
Library, Pennsylvania

Solvent extraction of tar acids from tar acid containing oils is of interest because of the potential savings in investment and operating costs over the conventional batch caustic extraction process. A relatively large number of solvents have been evaluated for this purpose. For the most part, preferred solvents contain a polar oxygen group⁽¹⁾ and include water, methanol, ethanol, formic acid, acetic acid, glycerine, triethylene glycol, and diethanolamine⁽¹¹⁾. Most of the previous studies involved countercurrent extraction with a single solvent. At high tar acid recovery levels, there is a significant carryover of neutral oil, requiring secondary purification of the polar solvent extract. Fractional extraction with two solvents provides a technique for the recovery of one component of a mixture both in high yield and in high purity.

Aqueous methanol-hexane were investigated in our laboratory⁽⁶⁾ as a solvent pair, based on their high selectivity for tar acids, low cost, ease of recovery, and stability. The yield and quality of tar acids produced by solvent extraction of the three most important commercial sources, coke oven tar, petroleum derived cresylic acids, and low temperature tar will be discussed. In addition, separation of tar acid isomers and homologues by solvent extraction will be described.

Experimental

Extraction studies were carried out in a 1" x 8' extraction column of the Scheibel type. A schematic diagram of apparatus is shown in Figure 1. The solvents, aqueous methanol and hexane were stored in 5-gallon borosilicate bottles. Gravity feed was used, flow rates being measured with rotameters. The temperature of the solvents was maintained by passage through coils heated or cooled in a water bath. Tar acid oil was pumped into the extraction column by means of a precision motor driven syringe. The tar acid oil feed point was the sixth stage of the twenty-eight stage extraction column. The methanol extract was freed of solvent by distillation on a 1" x 4' Vigreux column. The residue consisted of a mixture of water and refined tar acids. The water was separated by decantation and analyzed for dissolved tar acids by butyl acetate extraction. The wet tar acids were analyzed for water, neutral oil, and pyridine bases by standard methods. In the case of the tar acids derived from petroleum, aromatic thiols and disulfides were determined⁽⁵⁾. The hexane raffinate was similarly distilled. The solvent free residue was analyzed for tar acids by a modified caustic contraction method.

The detailed procedure for laboratory scale refining of a methanol extract with anion and cation exchange resins has been described⁽⁶⁾.

Discussion

Low Temperature Tar Acids

A tar acid oil (b.p. 160-230) derived from fluidized low temperature carbonization of a Pittsburgh Seam coal was refined with aqueous methanol-hexane. Previous studies⁽⁸⁾ narrowed the optimum concentration of methanol to 60 to 70%, using feed:methanol:hexane ratios of 1/1.5/3.0. The extraction conditions and results are shown in Table 1. The observed recovery of tar acids in the methanol extract was 92%. Neutral oil contamination was 0.08%, well below the acceptable level for commercial tar acids.

Tar base content was determined as 0.6%, which is 3 to 6 times higher than current specifications. This carryover of tar bases is a limitation of the solvent extraction approach to tar acid refining and is characteristic of all organic solvents considered to date. Removal of tar bases from tar acids by extraction with sulfuric acid or by distillation with sulfuric or phosphoric acids⁽¹⁾ has been proposed. An ion exchange technique, using a strong acid cation resin, for removal of tar bases from methanol extracts was developed in our laboratory and has already been described⁽²⁾.

Low temperature tar acids produced by solvent extraction or caustic extraction are contaminated with small quantities of aliphatic acid, ranging from acetic through butyric acid. These aliphatic acids are concentrated in the phenol fraction and impart a foul odor. Purification of the methanol extract with an anion exchange resin and a cation exchange resin in series^(2,7), results in the recovery of tar acids of satisfactory quality with respect to neutral oil, aliphatic acids, and pyridine bases.

A schematic flow diagram and the chemical reactions involved in this ion exchange purification are shown in Figure 2. The methanol extract is pumped over an anion exchange resin. The quaternary ammonium hydroxide groups combine with tar acids to form phenolate salts. The aliphatic acids by virtue of their higher acidity gradually displace the phenols until the resin is saturated with aliphatic acids. Breakthrough of aliphatic acids follows and regeneration is required. The methanol extract then contacts a cation resin where pyridine bases are removed as pyridinium sulfonates. The purified methanol extract is treated as before for the removal of methanol and water. The analysis of the fully refined tar acids is presented in Figure 2. The neutral oil and tar bases values of 0.08% and 0.05%, respectively, are well within commercial specifications. Aliphatic acids could not be detected by analysis or by odor.

Coke Oven Tar Acids

Solvent extraction of tar acids from coke oven tar presents a number of unique problems. A narrow boiling tar acid oil contains sufficient naphthalene to raise its freezing point well above ambient temperature, which necessitates diluting the tar acid oil with one of the solvents or extracting above ambient temperature. The concentration of tar acids is about 1/3 the concentration of the corresponding fraction from low temperature tar, and the ratio of tar bases is quite high, 0.11 as compared to 0.013 for low temperature tar acid oil. The low concentration of tar acids imposes an economic penalty, since throughputs and solvent ratios are proportional to the tar acid oil volume rather than absolute tar acid concentrations. The relatively high concentration of tar bases will result in a correspondingly large contamination of the recovered tar acids, since most

oxygenated solvents will extract pyridine bases. The detailed solvent extraction conditions and extraction results are shown in Table 2. A 90% recovery of tar acids was obtained. The neutral oil content of the recovered tar acids was well under 0.1%, which meets current specifications. The tar base contamination was 4.1% as compared to published specifications of 0.1 to 0.2%. Ion exchange purification would reduce the tar bases to an acceptable level. However, the costs for such a secondary purification would be quite high because the consumption of ion exchange regenerant is proportional to tar base concentration. The added refining costs might be justified if by-product credit could be taken for the tar bases, which can be recovered from the resin, free of tar acids and neutral oils.

Petroleum Cresylics

Crude tar acids produced by the caustic washing of gasoline have become an important source of refined cresylic acids in the U. S. Normally, these are available as caustic solutions containing 10 to 50% tar acids and from 1 to 20% aromatic mercaptans and disulfides. The conventional method of separating the sulfur compounds from tar acids is oxidation of the sulfur compounds to disulfides and separation of the caustic insoluble disulfides. While a significant purification can be effected, sufficient disulfides remain dissolved in the alkaline solution to be objectional, and there is a loss of tar acids during the oxidation step.

(a) Fractional extraction of a feed of this type with aqueous methanol-hexane under optimum conditions results in a recovery of 95% of the tar acids and simultaneous elimination of 99.5% of the mercaptans and disulfides in the feed. The effectiveness of this separation is quite unexpected when one considers phenol and thiophenol as prototypes of the mixture. Although thiophenol is almost a thousand times stronger an acid than phenol, thiophenol is rejected by aqueous methanol, the more polar solvent. The distribution behavior of thiophenols can be explained as a result of their inability to hydrogen bond with oxygenated solvents.

The details of an actual laboratory extraction of a crude tar acid mixture from petroleum is shown in Table 3. Using a tar acid/60% methanol/hexane volume ratio of 1.0/2/4.5, the recovery of tar acids in the extract was 97% and the sulfur compound contamination was 0.012%. Neutral oil contamination is 0.05%. Tar acids derived from catalytic cracking of gas oils contain very low concentrations of pyridine bases because chemical combination of basic compounds with the acidic cracking catalyst occurs during cracking. Maximum pyridine contamination is about 0.05%, which is acceptable.

Pitt-Consol Chemical Company, a subsidiary of Consolidation Coal Company, has operated a commercial extraction unit for the refining of petroleum derived tar acids for 6 years. Composite crude tar acids from at least 35 petroleum refineries are being processed. The performance of the commercial extraction column duplicates our laboratory unit in terms of yield and purity of refined tar acids.

Miscellaneous Refining Applications

Separation of Monohydric - Dihydric Phenol Mixtures

Tar acids boiling above 230°C from low temperature tar contain dihydric phenols, which turn pink when alkaline solutions of the tar acids are oxidized.

This discoloration is objectionable when disinfectant applications are contemplated. Removal of the pinking components has been effected by air-blowing alkaline solutions or extraction with borax, requiring consumption of chemicals and loss of some tar acids due to oxidation.

Fractional solvent extraction of the high boiling tar acids (230-350°C) produced from low temperature tar with more dilute methanol-hexane⁽¹⁰⁾, will separate the dihydric phenols. The results are summarized in Table 4. Using 30% methanol, 11% of the feed is recovered as a methanol extract, the raffinate boiling up to 260°C containing no dihydrics. An increase in the methanol concentration to 35% removed more of the dihydrics, the tar acids boiling up to 280° being free of pinking. When the methanol concentration was increased to 40%, a hexane raffinate of 79% was obtained, which showed no dihydrics in the tar acids boiling up to 300°C. Extraction of a synthetic mixture containing 50% catechol with 35% aqueous methanol-hexane produced a hexane raffinate, containing 76% of the monohydric phenols completely free of catechol. This method has the advantage of complete recovery of tar acids in two fractions, one of which contains no dihydric phenols.

Separation of 2,6-Xylenol From Mixed Cresols

An interesting application of aqueous methanol-hexane extraction is the separation of 2,6-xylenol from mixed cresols. 2,6-Xylenol occurs in low concentrations in the cresol fraction and is very difficult to recover in high purity because it boils quite closely to both o-cresol and m,p-cresol.

Fractional extraction of a mixture corresponding in composition to a fraction boiling between o-cresol and m,p-cresol was tried, using dilute methanol-hexane⁽⁹⁾. The results are presented in Table 5. When 45% methanol was tried, 2,6-xylenol was recovered in 63% yield and 67% purity. Dilution of the methanol to 35% resulted in increased selectivity, and 2,6-xylenol was recovered in 91% purity and 54% yield. It would require several precision distillations to accomplish the same result. Apparently, aqueous methanol, when sufficiently diluted, can separate tar acids on the basis of both acidity and molecular weight.

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Table 1

Solvent Extraction of Low Temperature Tar Acid OilFeed Composition (B.P. 150-230°C)

	<u>Wt. %</u>
Tar Acids	44.5
Neutral Oil	54.8
Tar Bases	0.6
Aliphatic Acids	0.2

Extraction Conditions

	<u>Vol. Ratio</u>
Tar Acid Oil	1.0
60% Methanol	1.5
Hexane	3.0

Composition and Yield of Methanol Extract

Yield of Tar Acids	92	Wt. %
		<u>Purity (Wt. %)</u>
Neutral Oil	0.08	
Tar Bases (Pyridine)	0.58	
Aliphatic Acids (Butyric Acid)	0.56	

Table 2

Solvent Extraction of Coke Oven Tar Acid OilFeed Composition (170-230°C)

	<u>Wt. %</u>
Tar Acids	14.3
Naphthalene	60.1
Neutral Oil	24.0
Tar Bases	1.6

Extraction Conditions

	<u>Vol. Ratio</u>
Tar Acid Oil	1.0*
70% Methanol	1.0
Heptane	3.0**

Purity of Tar Acids

	<u>Wt. %</u>
Neutral Oils	< 0.1
Tar Bases	4.1

*Fed as a 1:1 solution in heptane.

**Includes heptane used to dilute tar acid oil.

Solvent Extraction of Petroleum Cresylic AcidsFeed Composition (160-240°C)

	<u>Wt. %</u>
Tar Acids	82.2
Mercaptans) Thiocresols	16.3
Disulfides)	
Neutral Oils	1.5

Extraction Conditions

	<u>Vol. Ratio</u>
Tar Acid Oil	1.0
60% Methanol	2.0
Hexane	4.5

Purity of Tar Acids

	<u>Wt. %</u>
Neutral Oils	0.05
Tar Bases (Pyridine)	0.05
Mercaptans) (Thiocresols)	0.012
Disulfides)	

Table 4

Removal of Dihydric Phenols From High Boiling Tar Acids
230-350°CExtraction Conditions

Exp. No.	<u>1</u>	<u>2</u>	<u>3</u>
	<u>Feed Rates (ml/min.)</u>		
Tar Acids	4.5	4.5	4.5
Aqueous Methanol	12.0 (30%)	12.0 (33%)	18.0 (40%)
Hexane	10.5	10.5	10.5
<u>Yields (Wt. % Tar Acid Feed)</u>			
Methanol Extract	11	12	21
Hexane Raffinate	89	88	79

Table 5

Separation of 2,6-Xylenol From Mixed Cresols

	<u>Extraction Conditions</u>	
	<u>Vol. Ratio</u>	
Tar Acids	1	1
Aqueous Methanol	5 (45%)	10 (35%)
Hexane	10	5
Feed Composition		
o-Cresol	43.0	42.2
m-Cresol)	40.0	42.5
p-Cresol)		
2,6-Xylenol	17.0	15.3
Naphtha Raffinate Yield, (Wt.% Feed)	16.1	9.1
Composition, Wt.%*		
2,6-Xylenol	67.3	91.2
o-Cresol	19.1	8.8
m,p-Cresol	13.6	-

*Based on IR analysis.

FRACTIONAL SOLVENT EXTRACTION APPARATUS

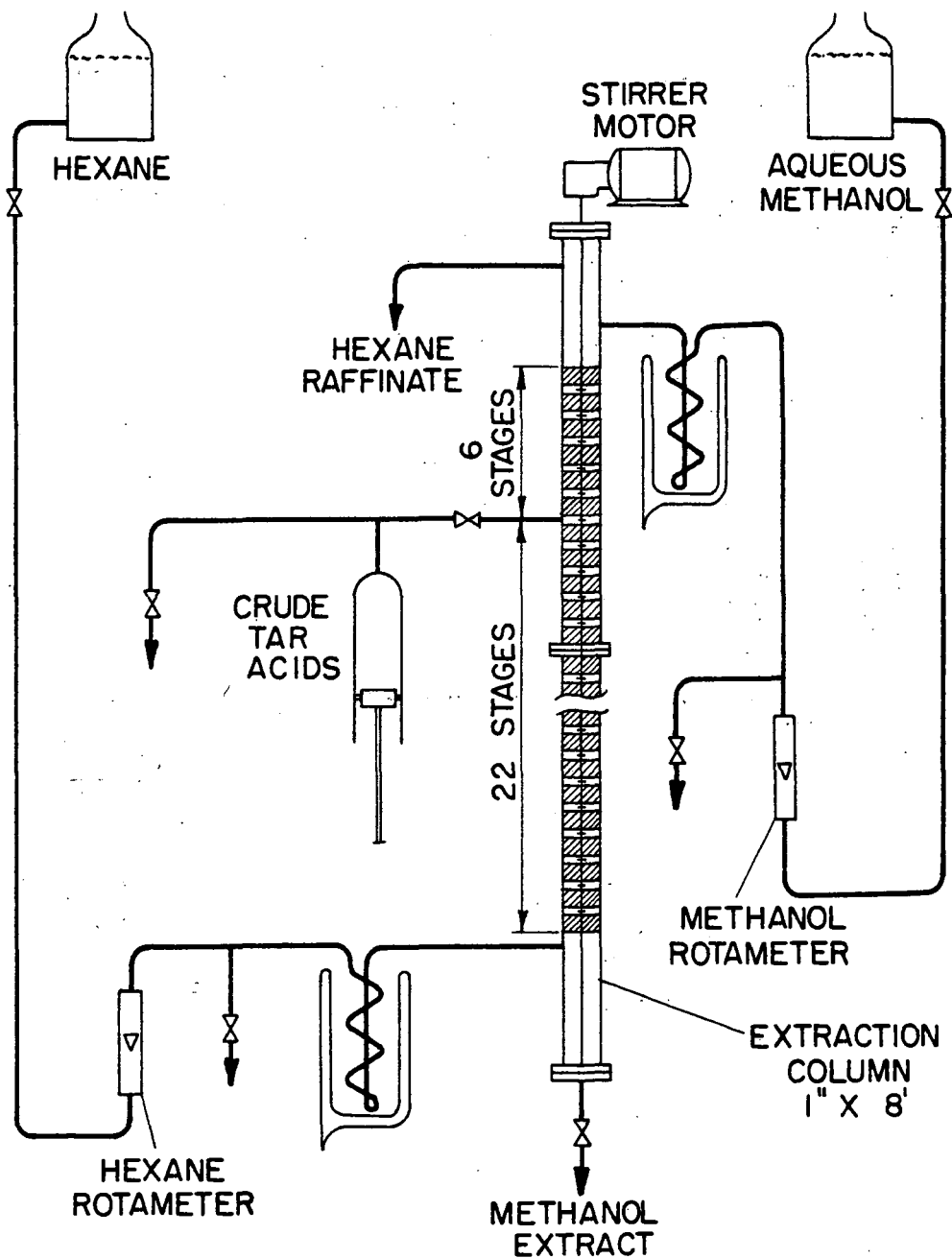
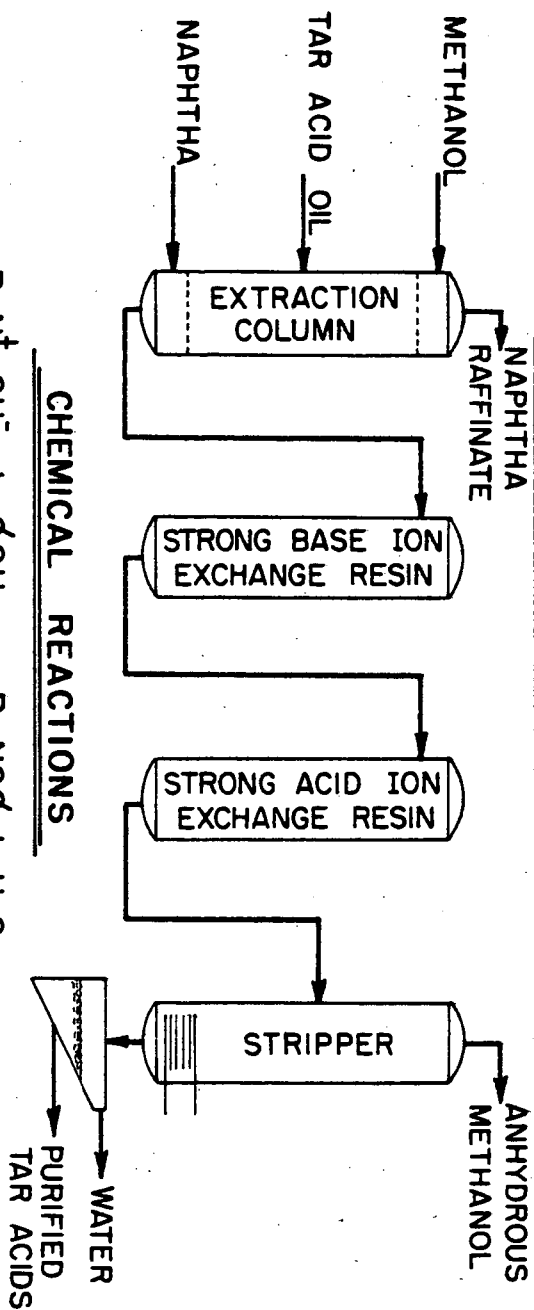
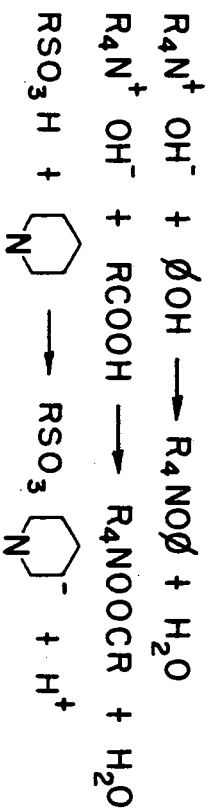


FIGURE 2

REMOVAL OF TAR BASES & ALIPHATIC ACIDS BY ION EXCHANGE REFINING



CHEMICAL REACTIONS



PURITY OF TAR ACIDS (Wt. %)

NEUTRAL OILS	0.08
TAR BASES (PYRIDINE)	0.05
ALIPHATIC ACIDS	Nil

Utilization of Coal Tar Bases

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The carbonization of coal gives rise to a complex mixture of hundreds of chemical compounds. Most of these compounds fall into one of three groups: hydrocarbons, acids, and bases. The coal tar bases are nitrogen compounds. The nitrogen atom is in the ring, as in pyridine, or it is attached to the ring as in aniline. Of the large number of compounds that are included in the category of coal tar bases, only pyridine and its simpler homologs are considered in this presentation.

Narrating the actual uses to which pyridines are put would be one way of discussing the utilization of coal tar bases. Perhaps a more stimulating approach is the one adopted herein, that is, a presentation of an outline of some chemical reactions of pyridines which are involved in their utilization.

Quaternization. Pyridine and the alkylpyridines react with alkyl halides, acid chlorides, and with alkyl or aryl sulfonic esters to form pyridinium salts. The rate of quaternization is influenced by the nature and position of the substituents on the pyridine ring. Methyl groups adjacent to the nitrogen decrease the rate of quaternization (127). The tendency to quaternize decreases in the order 4-picoline > 2-picoline > 2,4-lutidine > 2,6-lutidine. A method of purifying 2,6-lutidine from such contaminants as 3-picoline and 4-picoline, is based on the fact that 2,6-lutidine quaternizes much more slowly than do the picolines. The presence of a carboxyl group on the pyridine ring greatly retards the rate of quaternization. On the other hand, the esters of pyridine carboxylic acids are quaternized rather smoothly (118).

Pyridyl-pyridinium salts wherein the nitrogen atom of a pyridine nucleus is connected to a carbon atom at the 2-, 3-, or 4- position of a second pyridine molecule are known. N-pyridyl-4-pyridinium dichloride, made by the reaction of thionyl chloride upon pyridine (87) (21)(11), had been utilized in the preparation of 4- substituted pyridines (75). The recent contributions to the chemistry of pyridine-N-oxide have made N-pyridyl-4-pyridinium dichloride of less importance in the preparative methods (30).

2-Vinylpyridine reacts with pyridine hydrochloride to give an almost quantitative yield of 2-pyridylethylpyridinium chloride. The reaction is a general one, similar quaternary compounds are formed with pyridine thiocyanate, with quinoline hydrochloride, etc. 4-Vinylpyridine reacts in like manner (35).

Quaternary salts of pyridine, of alkylpyridines, as well as of other pyridine compounds may be oxidized by potassium ferricyanide to 1- substituted 2-pyridones (123). The nature of the substituent in the 3- position of a pyridinium salt determines whether ferricyanide oxidation gives a 2-pyridone or a 6-pyridone. If the 3- position is occupied by phenyl, 3-pyridyl, carboxy, or carboxy ethyl, 6-pyridones are formed. If the substituent is bromine, methyl, or ethyl, the oxidation occurs mainly at the 2- position. 3-Cyanopyridine methyl

iodide appeared to form both 2-, and 6-pyridones (22)(141). A more recent study of the ferricyanide oxidation of the quaternary of 1-phenylethyl-3-cyanopyridine does not confirm the presence of a 6-pyridone (144).

Methyl iodides of isonicotinic acid esters are oxidized with alkaline potassium ferricyanide to 4-carboxy-N-methyl-2-pyridone in yields up to 96% (55).

5-Alkyl-2-picolinium salts upon oxidation with iodine and pyridine and subsequently treating the resulting compound with dilute caustic give 1-substituted 5-alkyl-2-pyridones (14).

The pyridine-N-oxides also form quaternary compounds (82)(49). These compounds are important in the preparation of 2- and 4-substituted pyridines.

Oxidation. The inertness of pyridine towards oxidizing agents is one of its outstanding characteristics. Pyridine is not attacked by fuming nitric acid nor by chromic acid, and even potassium permanganate has but little effect on it.

In spite of its resistance to oxidation, pyridine may be oxidized quite readily to pyridine-N-oxide. The reaction is usually carried out with a mixture of hydrogen peroxide and acetic acid (67)(113)(115). The formation of the N-oxide linkage is a fairly general behavior of compounds containing the pyridine nucleus. Alkylpyridines form pyridine-N-oxides; so do alkanolpyridines (31)(17); and acetylpyridines (82)(129). Nicotinic acid, isonicotinic acid, and picolinic acids give the corresponding N-oxides (43)(59)(10), and so do their esters (82)(18), but 2,5-pyridine dicarboxylic acid is not oxidized to the N-oxide while its dimethyl ester is (118). The pyridine carboxamides also form N-oxides in the usual manner (57).

2-Bromopyridine-N-oxide and 2-bromo-6-methylpyridine-N-oxide are formed in good yields (3), and so are 3-bromopyridine-N-oxide and 3,5-dibromopyridine-N-oxide (57). 2-, 3-, and 4-pyridine sulfonic acids are resistant to oxidation by hydrogen peroxide and acetic acid. However, the sodium salts are readily converted to the corresponding N-oxides (47).

In contrast to the stability of pyridine, the alkylpyridines are attacked by a variety of oxidizing agents. The oxidation of the picolines, especially of the 3- and 4-isomers, to the corresponding pyridine carboxylic acids is one of their commercially more important reactions.

Potassium permanganate is used to convert the picolines to pyridine carboxylic acids (15)(98)(139). It is also useful in preparing 2-aminopyridine carboxylic acids from 2-aminopicoline (53) and 4-aminonicotinic acid from 4-amino-3-picoline (142). Potassium permanganate may be used to oxidize selectively a pyridine compound having more than one oxidizable group. An alkyl group in the 3-position is more readily oxidized than is one in the 4-position. 3,4,5-Trimethylpyridine oxidized with a 2% aqueous KMnO_4 gives 4,5-dimethylnicotinic acid and 4-methylnicotinic acid. 3,5-Dimethyl-4-butylpyridine forms 4-butyl-5-methylnicotinic acid and 4-butyl dinicotinic acid (148).

4-Methyl picolinic acid can be made from 2-styryl-4-methylpyridine by KMnO_4 oxidation at 0° to 5° C. (42); 4,5-diethyl picolinic acid from 2-styryl-4,5-diethylpyridine (91); 4-isopropyl-5-ethyl picolinic acid from 2-styryl-4-isopropyl-5-ethylpyridine (122). Treatment of 2-styrylpyridine at 200° C. with selenium dioxide gives 1-phenyl-2-(2-pyridyl)-1,2-ethane dione (24).

Nitric acid is an important commercial oxidizing acid. The picolines resist oxidation by nitric acid. Even at its boiling point nitric acid does not oxidize 3-picoline (121). Nitric acid at a temperature of about 230° C. and about 35 atms pressure oxidizes 3-

picoline to nicotinic acid (50% yield) and 4-picoline to isonicotinic acid (90% yield)(13).

A mixture of nitric acid and sulfuric acid or phosphoric acid gives good yields of pyridine carboxylic acids from picolines. The reaction proceeds at atmospheric pressures (39).

Sulfuric acid, with selenium as a catalyst, may also be used to oxidize picolines to pyridine carboxylic acids (155). The oxidation of 2,4-lutidine with sulfuric acid plus selenium gives 29% of 2,4-pyridine dicarboxylic acid and 18% of 2-methylisonicotinic acid (116).

Pyridine carboxylic acids can be produced by the catalytic vapor phase air oxidation of picolines (37). The position of the methyl group determines the ease of oxidation; the methyl group in the 3-position is the most resistant to oxidation (36).

Vapor phase oxidation of picolines with air in the presence of ammonia or an amine yields cyanopyridines. This method of making cyanopyridines was first observed in the vapor phase oxidation of nicotine wherein 3-cyanopyridine was made (38). 3-Picoline is converted to 3-cyanopyridine by oxidation with sulfur in the presence of ammonia (143).

Recent studies on the oxidation of picolines with selenium dioxide show the ease of oxidation to be 4-picoline > 2-picoline > 3-picoline. In fact, 3-picoline is not affected by SeO_2 and hence is used as a solvent for carrying out the oxidation of the other picolines. 2,5-Lutidine gives 79% of 3-methyl picolinic acid. 2,4-Lutidine gives a mixture of 2-methyl isonicotinic acid (44%) and 2,4-pyridine dicarboxylic acid (76).

Picolinic acid has been prepared by the liquid phase oxidation of 2-picoline with gaseous oxygen in the presence of a copper salt of a fatty acid (65); similarly isocinchomeric acid was made from aldehyde collidine and isonicotinic acid from 4-picoline (134).

3-Picoline has been oxidized electrolytically to nicotinic acid (89).

Alkylpyridines may be oxidized to the corresponding aldehydes by vapor phase oxidation in the presence of a large excess of water vapor. 2-Picoline gives 2-pyridine aldehyde (106); 2,6-lutidine may give 6-methyl-2-pyridine aldehyde, 2,6-pyridine dialdehyde (107) and 6-carboxy-2-pyridine aldehyde (103); 3,5-lutidine forms 5-methyl-3-pyridine aldehyde (105).

It has been reported that 2-picoline may be oxidized to 2-pyridine aldehyde by means of selenium dioxide (99)(66)(20).

Useful laboratory methods for the preparation of pyridine aldehyde involve the oxidation of pyridyl carbinols with manganese dioxide (64), selenium dioxide (77), or lead tetracetate (111). 2,6-bis-Hydroxymethylpyridine is oxidized by SeO_2 to 2-hydroxymethyl-6-pyridine aldehyde (104). The 3-pyridylaldehyde has been prepared by vapor phase oxidation of 3-pyridyl carbinol (69).

3-Pyridine aldehyde, 4-pyridine aldehyde, and 6-methyl-3-pyridine aldehyde were prepared in good yield by reducing 3-cyanopyridine, 4-cyanopyridine, and 6-methyl-3-cyanopyridine with semi-carbazide hydrochloride and Raney Nickel, and liberating the aldehyde from the resulting aldehyde semicarbazone by acid hydrolysis in the presence of meta nitrobenzaldehyde (50). 3-Pyridine aldehyde in 83% yield has also been made by the reduction of 3-cyanopyridine with $\text{NaHA}(\text{OEt})_3$ (73).

Isonicotinaldehyde has been made by the ozonization of 4-styrylpyridine (152); 2-pyridine aldehyde by the ozonization of 2-vinylpyridine (25).

Hydrogenation. In contrast to its inertness towards oxidation, pyridine is rather easily hydrogenated. The complete reduction of

pyridine to piperidine, i.e. its hexahydro derivative, is a commercial operation of many years standing.

Various catalysts are useful in reducing pyridine with hydrogen. Nickel catalysts, especially Raney Nickel, are suitable for the formation of piperidine (5). To avoid hydrogenolysis with the formation of high-boiling by-products, the temperature is kept as low as possible (78). The alkylpyridines are readily reduced by hydrogen (Raney Nickel catalyst) to the corresponding alkylhexahydropyridines (5)(130)(80).

Platinum oxide is a useful catalyst for the laboratory hydrogenation of pyridines. Pyridine poisons platinum oxide catalyst. However, the hydrogenation of pyridine hydrochloride, or of quaternary salts of pyridine proceeds very well (61). The slow rate of hydrogenation of the base itself may be due to the free electrons on the nitrogen. Through these electrons the pyridine forms a compound with the catalyst thereby withdrawing the platinum from its role of a catalyst. In the quaternary salts, the pyridine electrons are tied up, thereby permitting the hydrogenation to proceed many times faster than if free pyridine were used (108). The pyridine when dissolved in acetic acid can be hydrogenated with platinum oxide (54).

Piperidine manufactured by the electrolytic reduction of pyridine contains substantial quantities of tetrahydropyridine; the piperidine produced by hydrogenation over Raney Nickel contains no appreciable amount of the 1,2,5,6-tetrahydropyridine (45). Electrolytic reduction of 2-methylpyridine gives 2-methylpiperidine and 24.4% of 2-methyl-1,2,3,6-tetrahydropyridine; 3-methylpyridine gives 3-methyl-1,2,5,6-tetrahydropyridine in addition to 3-methylpiperidine; and 4-methylpyridine gives 4-methylpiperidine and 4-methyl-1,2,3,6-tetrahydropyridine (51). The electrolytic reduction of quaternary pyridinium salts gives the same types of products so far as the position of the double bond is concerned (52).

In the laboratory, sodium and absolute alcohol are frequently used to reduce pyridine to piperidine (102). This reaction was discussed in 1884 by Ladenburg (90). It is important that the alcohol be dry. If 95% ethanol is used, little or no piperidine is produced but instead the pyridine ring is ruptured and ammonia evolved (136) (137). Reducing 3-methylpyridine with sodium and absolute butanol gives in addition to 3-methylpiperidine, 28.4% of 3-methyl-1,2,5,6-tetrahydropyridine; 4-methylpyridine gives 45% of 4-methyl-1,2,3,6-tetrahydropyridine in addition to 4-methylpiperidine (51). A number of 4-alkylpiperidines were prepared from 4-alkylpyridines by reduction with sodium and butanol followed by hydrogenation with hydrogen in the presence of palladium. The sodium-butanol reduction gave mainly the tetrahydropyridine which was converted to the piperidine by hydrogen (149).

Reduction of pyridine with LiAlH_4 gives 1,2-dihydropyridine (19). LiAlH_4 reduction of quaternary salts of alkylpyridines gives only the tetrahydropyridines (51).

Pyridine carboxylic acid esters are reduced, in good yield, by LiAlH_4 to the corresponding hydroxymethylpyridines (79)(112)(81); but their quaternaries with LiAlH_4 give 1-alkylhydroxymethyl-tetrahydropyridines (51).

Catalytic hydrogenation (Ni catalyst) of pyridine in various aliphatic alcohols (1 to 16 carbon atoms) gives the corresponding 1-alkylpiperidine in yields in excess of 70% (133).

Amination. Because of the difficulty of nitrating pyridine, the usual methods for the synthesis of aromatic amines are not available for the preparation of aminopyridines. The nitration of pyridine proceeds only under drastic conditions, fuming sulfuric acid and potassium nitrate plus a temperature in excess of 300°C .; the nitro group enters

the 3- position; the yield is only 15% (84). When especially high temperatures are used, the nitro group occupies the 2- position (46). Poly-alkylpyridines are somewhat easier to nitrate, the reaction conditions are milder, and the yields are better (120).

While pyridine is difficult to nitrate, pyridine-N-oxide is readily nitrated; the nitro group enters the 4- position (115). The nitration can be carried out at water-bath temperatures with a mixture of nitric and sulfuric acids; the yield is above 80% (83). The ease of nitration extends to the alkylpyridine-N-oxides and to various derivatives of pyridine-N-oxide.

The 4-nitropyridine-N-oxides are readily reduced and deoxygenated to the corresponding 4-aminopyridines. Various reducing agents have been used, e.g. iron and acetic acid (115), hydrogen with Raney Nickel (41)(63), hydrogen with palladium in acetic anhydride (48). 4-Nitropyridine-N-oxides offer a good route to 4-aminopyridines.

Prior to the 4-nitropyridine-N-oxide approach to the synthesis of 4-aminopyridine, it was prepared by the Hofmann degradation of isonicotinamide (93)(114) or from 4-pyridyl pyridinium dichloride and ammonium hydroxide (87)(6). The latter method has also been used for making 4-amino-3-methylpyridine (44).

The most convenient method for preparing 3-aminopyridine is from nicotinamide (7); it may also be prepared from 3-bromopyridine and aqueous ammonia in the presence of copper sulfate (97).

In 1914 the Russian chemist, Chichibabin, discovered a most interesting and useful reaction for introducing an amino group onto the 2- position of the pyridine nucleus. He found that pyridine reacts with sodamide to form 2-aminopyridine (92). The amino group goes almost exclusively into the 2- position, only a trace of 4-aminopyridine is formed; no 3-aminopyridine is found.

2-Aminopicolines may be prepared by reacting the picolines with sodamide (135). In the case of 3-picoline, the two carbon atoms adjacent to the nitrogen are different because of their relation to the 3-methyl group. Sodamide gives two aminopicolines when it is reacted with 3-picoline, that is, 2-amino-3-picoline and 6-amino-3-picoline; the former predominates (34).

Pyridine and 2-picoline have been aminated in the alpha position with alkylamines by refluxing the pyridine with a slight excess of the alkylamine and a stoichiometric amount of sodium (88).

Alkylation. There are several interesting reactions available for the alkylation of the pyridine ring. Arens and Wibaut found that an alkyl group may be introduced onto the 4- position of pyridine by the action of zinc dust on a mixture of pyridine, an organic acid anhydride and the corresponding organic acid (9)(56). This reaction is not applicable to alpha substituted pyridines; it cannot be used to introduce an alkyl group onto the 4- position of 2-picoline, 2-aminopyridine, picolinic acid, nor of 2-chloropyridine (153). The reaction proceeds in a "normal" manner with 3-picoline (140). Iron powder may be used in place of zinc dust (154).

At the Reilly Laboratories we found that pyridine as well as alkylpyridines may be alkylated by the use of aliphatic acid salts of tetravalent lead (128). By this means alkyl groups containing one less carbon atom than the acid radical of the lead salt are produced; the alkyl group enters both the 2- and the 4- positions if they are open. The reaction of 3-butylpyridine with lead tetra-acetate gives a mixture of 3-butyl-2-methylpyridine (15%), 5-butyl-2-methylpyridine (5%), 3-butyl-2,6-dimethylpyridine (1.5%), and 3-butyl-4-methylpyridine (5%) (62).

Lithium alkyls and phenyl lithium are used to introduce an alkyl or phenyl group onto the 2- position of pyridine (156), of 3-picoline

(1), of 3-aminopyridine and 3-methoxypyridine (2).

In 1936 Chichibabin described the alkylation of 2-picoline and of 4-picoline by reacting the picolines with sodamide to form picolyl-sodium and reacting the latter compound with an alkyl halide (29). The activity of the hydrogen atoms in the methyl groups of 2- and 4-picoline is ascribed to the ability of these picolines to take part in resonance with the azomethine linkage of the pyridine ring. Since 3-picoline cannot participate in such resonance, it was long believed that 3-picoline could not be alkylated by the Chichibabin method. In 1951 Brown and Murphey (23) showed that 3-picoline may be alkylated by the sodamide method.

The Chichibabin method of alkylating picolines is of general applicability, both the lower alkyl halides as well as long chained ones may be used (86). Substituted picolines may be alkylated (101)(8)(132)(26).

2,4,6-Collidine presents an opportunity of attaching an alkyl group on either of the alpha methyl groups or onto the methyl group in the 4-position. We found that the sodamide method introduces the alkyl onto the 4-methyl group (33). 2,4-Lutidine is also alkylated at the 4-position (95).

Ziegler and Zeiser (156) showed that phenyl-lithium reacts with 2-picoline to form 2-picolyl-lithium which may be reacted with alkyl-halides to attach an alkyl group onto the 2-methyl group. This reaction has been applied to the preparation of a number of 2-picolyl compounds. With 2-bromopyridine there is formed 2,2'-dipyridylmethane (117). With chloroacetylenes, 2-pyridylacetylenes are prepared (58). 1-(2-Pyridyl)-4-chloro-3-pentene was made from 1,3-dichloro-3-butene (72). 2-Pyridylmalondinitrile was made from N-methyl-N-cyanoaniline (94).

In contrast to the ease of introducing groups onto the 4-methyl group through the intervention of sodamide, attempts to use the lithium method have not been too satisfactory (117). The usual manner of making 2-picolyl-lithium is to prepare a solution of phenyl lithium and then add 2-picoline to this solution. In the alkylation of 4-picoline, better results are obtained when the phenyl-lithium is added very slowly to the 4-picoline (151).

Alkylation of 2,4,6-collidine by the sodamide process proceeds mainly at the 4-position. Alkylation by the lithium method gives mainly 2,6-dialkyl-4-methylpyridine and a lesser amount of 2,4,6-tri-alkylpyridine (74).

Alkali metals are used as catalysts in the alkylation of 2-picoline and 4-picoline with compounds containing an ethylenic double bond. A mixture of 2-picoline, sodium, and ethylene under 60 atms. pressure heated to 120-130° gives a mixture of 2-propylpyridine (23%) and 2-(3-pentyl)pyridine (126)(119). Under similar conditions 2-picoline and butadiene give 2-(3-pentenyl)pyridine and 2-(5-nondienyl-2,7)pyridine; styrene and 2-picoline give 1-phenyl-3-(2-pyridyl)propane (150). Acrylonitrile reacts with 2- and 4-picolines in the presence of a bit of sodium to give pyridyl-butyronitriles and dicyanopyridyl pentanes (32)(26).

Picolines with methyl groups in the 2- or 4-position may be alkylated in the vapor phase by reaction with aliphatic aldehydes (40).

Condensation. The reaction of picolines with aldehydes may be considered a classic in the pyridine series. The methyl groups in the 2- and the 4-position are reactive, whereas a methyl group in the 3-position is not.

2-Picoline condenses with formaldehyde to give 2-ethanolpyridine (85); 4-picoline gives 4-ethanolpyridine (124).

2,4,6-Collidine presents a situation wherein the formaldehyde

must decide whether it will react with the methyl group in the 4-position or with one of the alpha methyl groups. In the presence of a large excess of 2,4,6-collidine, the formaldehyde condenses almost exclusively with a methyl group in the 2-position; only a trace of the 4-ethanolpyridine is formed (109). In the presence of a large excess of formaldehyde, the 4-methyl group as well as both alpha methyl groups react (96)(16). 2,4-Lutidine also reacts with formaldehyde, preferentially at the 2-position (110)(42).

4-Ethylpyridine has been condensed with formaldehyde (excess) to give a mixture of dimethylol-4-ethylpyridine (65.5%) and of monomethylol-4-ethylpyridine (26.6%)(131).

The introduction of the -N-oxide group enhances the activity of picolines towards condensation reactions. Neither 2- nor 4-picoline will condense with ethyl oxalate, but their -N-oxides readily condense with ethyl oxalate to give the corresponding pyruvates (4).

Studies in our laboratory show that the presence of a chlorine in the 2-position of 4-picoline retards the condensation activity of the methyl group. 4-Bromo-2-picoline reacted with formaldehyde to give only a 9% yield of the corresponding ethanolpyridine (25).

To improve the yield of 2-(2-hydroxyethyl)-3-picoline, the 2-lithio derivative of 2,3-lutidine was reacted with paraformaldehyde. 2-Picolyl-lithium reacts smoothly to give 2-ethanolpyridine (54). 2,6-Lutidine through its 2-lithio derivative has been condensed with propionaldehyde to give a good yield of 2-(2-hydroxybutyl)-6-methylpyridine (68).

2-Picoline and 4-picoline readily condense with benzaldehyde and with substituted benzaldehydes. With benzaldehyde, it is difficult to stop the reaction at the ethanol stage because of the ease with which this alkine dehydrates to stilbazole. If it is desired to stop at the alkine stage, it is suggested that the picoline be condensed with the benzaldehyde in the presence of water and that no condensing agent be used (138). The yield of alkine is increased by replacing a hydrogen of the methyl group of 2-picoline with magnesium and condensing the resulting 2-picolyl magnesium chloride with benzaldehyde (100).

Stilbazoles are the products usually obtained by the condensation of aromatic aldehydes and 2-picoline and 4-picoline. In general, the reaction is carried out by refluxing a solution of the aromatic aldehyde, the picoline, and acetic anhydride (138)(28)(60). Yields above 90% are not uncommon (71).

Since 3-picoline does not condense with aldehydes, 3-stilbazole cannot be made as are the 2- and 4-stilbazoles. 3-Stilbazole has been made by condensing 3-pyridyl acetic acid with benzaldehyde and then decarboxylating the resulting beta-phenyl-alpha-3-pyridyl acrylic acid (12). The methyl iodide quaternary of 3-picoline condenses with benzaldehyde in the presence of piperidine to give a small yield of the alkine (75).

Benzaldehyde condenses with 2,4-lutidine by adding a molecule of the aldehyde to each of the methyl groups to give 2,4-distyrylpyridine (60)(110) and also to give 2-styryl-4-methylpyridine (42). 2,6-Lutidine condenses with benzaldehyde to give a mixture of 2-methyl-6-styrylpyridine and 2,6-distyrylpyridine (70).

The hydrogens of the methyl groups in 2- and 4-picoline are comparable in reactivity to those of the methyl ketones. And, as would be expected, the Mannich reaction applies to these compounds. 2-Picoline condenses with formaldehyde and diethylamine to give 2-(beta-diethylaminoethyl)pyridine (145).

Formaldehyde in an alkaline medium reacts with 3-hydroxypyridine to yield 2-hydroxymethyl-3-hydroxypyridine (146); 2-methyl-5-hydroxypyridine gives 2-methyl-5-hydroxy-6-hydroxymethylpyridine, indicating the influence of the hydroxyl group is more dominant than that of the

alpha methyl group (147). With Benzaldehyde, 2-methyl-3-hydroxypyridine in an acid medium gives 2-styryl-3-hydroxypyridine (75).

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Tar Acid Extraction in a Rotating Disc Contactor

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The extraction of coal tar acids from tar acid oils by means of caustic solutions was investigated in a 4 in. I.D. Rotating Disc Contactor extraction column. This investigation was one phase of a program directed towards the modernization of the coal tar processing plant at Pittsburgh Coke and Chemical Co. Subsequent changes in the economic picture for coal tar derivatives led to a cancellation of the projected modernization.

Two feed stocks from independent manufacturing sources each containing 14-16 wt.% tar acids in neutral oil were employed in the test series. The extracting solution was fresh 9 wt.% caustic in water. These represented the projected plant operating conditions near capacity operation. The tar acid in neutral oil system is chemically indeterminate. Tar acid is a generic name for a mixture of phenol, cresols, xylenols etc. Neutral oil is a mixture of methyl naphthalene, naphthalene, alkyl benzene etc. The acid-oil ratio and the individual constituent ratios are functions of the coal and the coking conditions. Wide variations were normally encountered using local feed stocks which variations were expected to be compounded when outside sources were employed as capacity operation was approached. The 14-16% acid content represented the maximum likely to be encountered over any extended period.

The study also covered the benzene-acetone-water system in order to provide a reference base for the column performance.

The performances of the RDC column are reported for both ternary systems. Certain aspects of the results must be viewed with caution. The measured relative changes in column performance with changes in the levels of the operating variables are believed to be accurate. However, uncertainties with respect to the tar acid equilibrium phase data and its interpretation coupled with the proximity of the operating line to the equilibrium line in these studies make the absolute values of the transfer stage height for this system rather doubtful.

Ternary phase equilibrium data have been published for the benzene-acetone-water system¹. No data concerning the tar acid oil-aqueous caustic system have been published. The detailed development of the ternary phase diagram for the tar acid oil-caustic system is not reported in this paper. However, some discussion of the approach and the results is essential to the evaluation of the results of the column tests.

Experimental

Absolute analytical techniques for both the tar acid content of, and the species distribution in the feed stock, have not been developed to the point where they are practical on a semi-routine basis. An infrared technique for measuring the

(1) Briggs, Comings, Ind. Engr. Chem. 35, 411 (1943).

concentration of the OH groups was developed which is believed to be fairly reliable². The total weight of acid is then calculated by using an arbitrary molecular weight which agrees with long term plant experience.

Tar acids in the caustic phase were determined by potentiometric titration with HCl to a pH of 8 in alcoholic solution.

The phase boundaries in part and the tie lines were obtained by mixing known weights of tar acid oil and 9 wt.% caustic and analysing the phases for acid distribution. The phase boundaries for a number of feed stocks obtained over a two month period were determined by cloud point titrations according to the method of Othmer³. The phase boundary locations for some four feed stocks and a synthetic feed of phenol in naphthalene were very similar over the temperature range between 80° and 95°. Tie line data scatter rather badly. No positive trend in slope or location as a result of composition or temperature differences could be seen. These data suggest that normal in-plant variations of feed composition should not affect the extraction column performance significantly. A generalized phase diagram was synthesized from all these data.

The column tests were carried out at a later date using two feed stocks which were not a part of the above study. However, the generalized diagram was assumed to apply to the new feeds. This approximation is reasonable in view of the similarity of phenol and cresols with respect to their reactions with caustic. This approximation may not be safe if the concentration of the caustic changed appreciably.

The basic unit of the Rotating Disc Contactor is a cylindrical cell baffled at each end and stirred by a centrally located solid disc. The cells of the pilot column had the following dimensions:

ID	4 in.
Height	2 in.
End baffles	4 in. OD, 3 in. ID, 1/8 in. thick
Rotating disc	2 1/4 in. D, 1/4 in. thick

The early benzene-acetone-water studies and the tar acid extraction studies were carried out in a glass walled column containing 24 cells. The later benzene-acetone-water studies were executed in a stainless steel column containing 36 cells.

Feed and effluent rates were controlled by rotameters. The effluent rates for the tar acid studies are based on continuous weight measurement. The solids precipitated during the acid extraction quickly rendered the rotameters nearly opaque and may have caused some sticking. As a result the use of weigh tanks was adopted.

The interface was sensed and controlled by means of capacitance probes. Solids deposition on the probes during the tar acid extraction forced some modification to the detector system. Two side mounted sight glass chambers were installed with the probe wires wrapped around the outside of the glass at the desired level. Alternate cleaning of the inside of the glasses every 20-30 minutes was found to be satisfactory. After the completion of the column studies a flow system interface detector was developed which was not subject to the problems associated with solids deposition.

The column and auxiliary equipment were steam traced throughout.

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- (3) Othmer, D. F. et al, Ind. Engr. Chem. 33, 1240 (1941).

Discussion

The initial dispersion of the phases is generally achieved with the aid of a mixing nozzle. The intensity of interfacial turbulence is probably a maximum at this point. The mean droplet size may be a minimum. The excess mechanically induced turbulence dies out very rapidly and constant relative velocities are approached within a few inches up the column. Where only a few transfer units are attainable in the extraction column a significant fraction of the transfer can occur over this stage. Coalescence of the droplets begins almost immediately after leaving the nozzle.

Performance of the mixing system is one reason why a decrease in the height of a transfer stage is obtained with increasing total throughput when the number of total stages involved is small.

The coefficients of heat or mass transfer per unit area of interface have been shown to depend primarily on the settling rate of the droplets⁴. In stirred systems of this nature the accelerations imposed by the stirrer are a small fraction of that due to gravity. The rate of the stirrer in an RDC column or packing in a packed tower, is therefore the maintenance of a minimum droplet size spectrum. Stirring breaks down the droplets to a size spectrum which appears to depend on the power input per unit volume⁵. The coefficient of mass transfer per unit area falls off at a slower rate than the surface area increases with increasing stirrer speed⁴. That is, the quantity transferred across the interface per unit volume of stirred vessel increases with stirrer speed.

The importance of internal mixing within, and new surface generation on, the droplets as a result of coalescence and breakdown has not been resolved.

In many two phase systems, mixing of the phases at conditions other than equilibrium results in spontaneous interfacial turbulence. Spontaneous emulsification has been observed in a few systems. Random concentration fluctuations along the interface produce viscosity, density, and surface tension gradients. The surface expands and contracts locally. This movement couples with gravity induced convection currents due to density gradients to produce convection cells at the interface^{6,7}.

Spontaneous interfacial turbulence could be detected under certain conditions with both of the systems under study. The acetone-benzene-water system exhibited turbulence only when the conditions were such that the local solution density could be greater than the liquor density below it. Whether this restriction applies to the phenol in naphthalene-caustic system is not certain. The cell sizes appeared to lie between 0.03 and 0.1 in. diameter.

The mean drop size observed with the benzene-acetone-water system in the RDC column was not more than 3 times the size of the cells observed above at flat interfaces. At such low drop size to convection cell size ratios, development of these convection cells might not be possible.

The presence of surface active agents at the interface does not inhibit normal molecular diffusion. The intrinsic mass transfer coefficient involves both

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- (5) Reman, G.H., Olney, R.B., Chem. Engr. Prog. 51, 141 (1955).
- (6) Sterling, C.V., Scriven, L.E., A. I. Ch. E. Journal 5, 514 (1959).
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turbulent and molecular diffusion. This coefficient has been found to be reduced by the subclass of surface active agents which rigidize the interface^{4,8}.

Not generally realized is the ability of traces of solids to rigidize an interface. Distilled water exposed to the atmosphere for a few minutes develops a marked surface rigidity as a result of dust deposition⁹. One of the authors has noted the same phenomena with a number of organic compounds.

The benzene-acetone-water system is believed to be free of surface active agents and should be free of solids. However, the extent of the formation of solid precipitates at the interface during extraction of tar acids is such that major reductions in the mass transfer coefficient could have occurred.

The experimental values of the transfer stage height are shown on Figure 1 and 3 for the benzene-acetone-water system and on Figures 2 and 4 for the tar acid in oil-caustic system.

The only significant process variable appears to be the rotor speed both for the benzene-acetone-water and the tar acid in oil-caustic system. For the first system neither the direction of transfer of the acetone, the phase which was dispersed, nor the throughput had significant effects on the number of transfer stages. The flooding point did however depend on the phase which was dispersed, Figure 5. The same pattern was observed with the tar acid in oil-caustic system over the limited ranges studied.

These data suggest that such phenomena as interfacial turbulence, surface rigidity induced by solids accumulation at the interface, and the direction of mass transfer are not normally important variables. The volumetric mass transfer coefficient appears to depend primarily on the droplet size spectrum attainable in the system. However, capacity does depend on the particular phase which is dispersed.

The reader is again cautioned against using the HTS values obtained for the tar acid in oil-caustic system for conditions other than reported. The operating lines tend to pinch the equilibrium curve, Figure No. 4, and the exact location of the equilibrium curve is uncertain. Depending on the individual interpretation of the data, a 50% difference in the number of transfer stages may be obtained. However, the location of the curve, while it changes the numerical values, does not change the observed dependence of the numbers of the operating variables.

One of the surprising features of the RDC column performance is the absence of solids build-up within the stirred zones. The machine might be capable of handling slurries. In general, the Rotating Disc Contactor develops a high transfer rate per unit volume, and is insensitive to small upsets in the feed system, and can tolerate significant quantities of solids within the column proper.

(8) Davies, J. T., Mayers, G. R. A., Chem. Engr. Sci. 16, 55 (1961).

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RDC EXTRACTION COLUMN PERFORMANCE

24-36 CELLS 4 in. I.D. 2 in. H. STIRRER DISC 2 1/4 in. D

FIGURE No. 1

TRANSFER OF ACETONE BETWEEN
BENZENE AND WATER

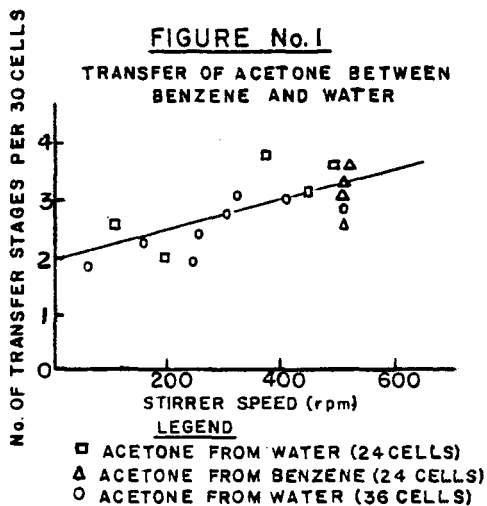


FIGURE No. 2

TRANSFER OF TAR ACIDS INTO
CAUSTIC

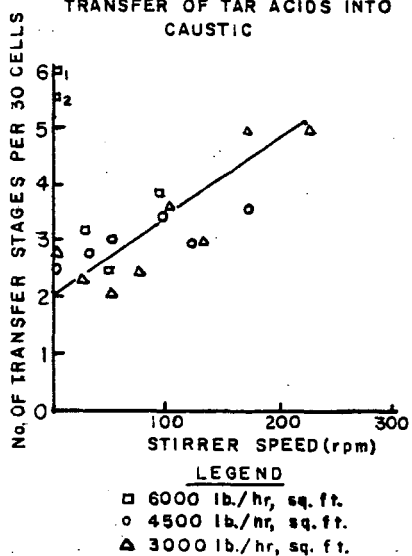


FIGURE No. 3

BENZENE-ACETONE-WATER
EQUILIBRIUM DATA

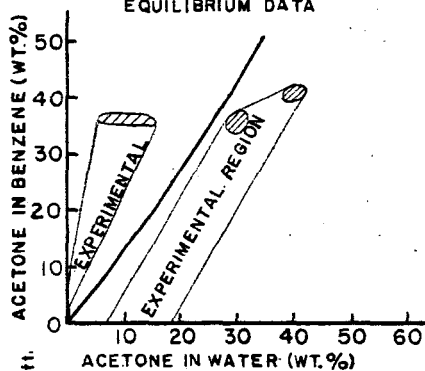


FIGURE No. 4

NEUTRAL OIL-TAR ACIDS- 9wt. % CAUSTIC
SOLUTION EQUILIBRIUM DATA

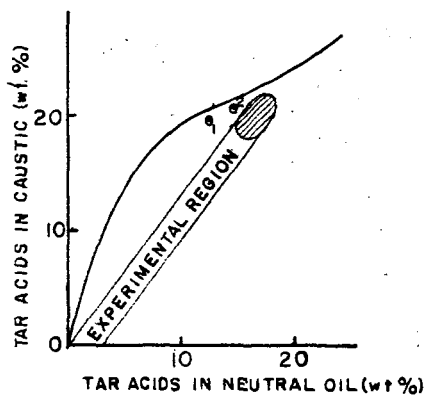
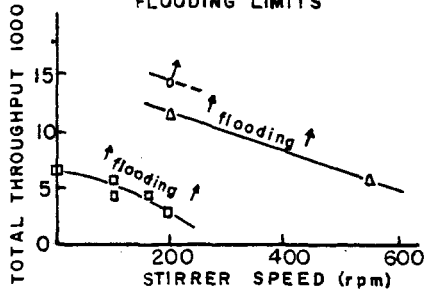


FIGURE No. 5
FLOODING LIMITS



LEGEND

- TAR ACIDS DISPERSED PHASE
- △ BENZENE DISPERSED PHASE
- WATER DISPERSED PHASE

TABLE I

Extraction of Tar Acids with 9 wt. % NaOH in Water. Feed to Solvent ratio 1.9 to 2.1. Tar Acid Oil dispersed phase.

Column Temperature °C	Rotor Speed rpm	Total Throughput lb./hr., sq.ft.	Tar Feed wt. %	Acid Content Extract wt. %	NaOH in Solvent wt. %	No. of Transfer Stages
86	0	4700	14.9 [*]	19.4	9.7	2.0
87	25	4100	14.9 [*]	20.7	9.7	2.3
87	50	5000	14.9 [*]	21.0	9.7	2.5
85	75	4100	14.9 [*]	21.0	9.7	2.8
86	123	4100	16.8	20.2	9.2	2.5
88	165	4100	16.8	21.8	9.2	3.0
92	0	6800	12.5 [*]	20.5	9.2	5.0
88	0	5800	14.3 [*]	22.0	9.2	4.5
85	25	6300	16.8	23.0	9.8	2.7
85	50	6000	15.4	22.5	9.9	2.1
85	76	5800	17.4	23.5	9.6	3.2
86	0	3200	15.9	19.9	8.9	2.2
86	25	3400	15.9	19.5	8.8	2.1
84	50	3200	16.5	19.8	9.4	1.7
85	75	3300	16.5	21.0	9.2	2.1
85	100	3200	16.5	20.9	9.1	2.9
87	125	3100	16.5	20.3	9.1	2.5
85	171	3200	16.5	20.9	9.2	4.0
85	230	3100	16.5	22.2	9.5	4.0

* Synthetic of Wilton Still Tar Acid Oil and recovered Tar Acid from plant.

TABLE II

Transfer of Acetone between Benzene and Water at 23°C

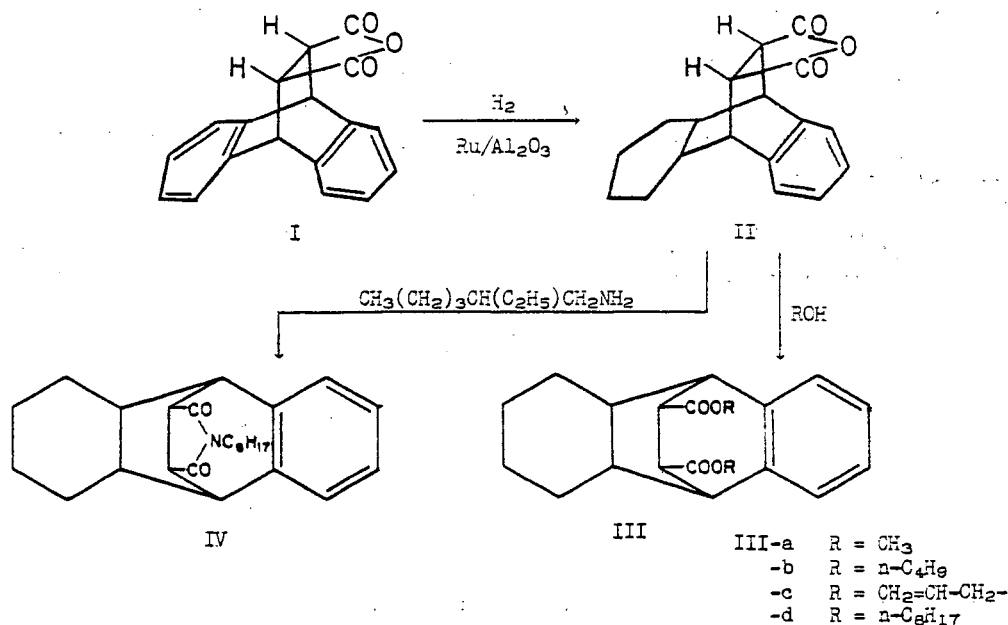
Continuous Phase	Rotor Speed	Phase Throughput		Acetone Content		Raffinate	Transfer Stages
		Benzene	Water-Acetone	Feed Water-Acetone	Extract Benzene-Acetone	Water-Acetone	
	rpm	lb./hr., sq.ft.		Wt. %	Wt. %	Wt. %	No.
Benzene (24 cells)	100	350	650	40.5	41.9	15.1	2
	180	350	650	41.3	40.9	19.5	1.5
	375	350	650	39.6	41.8	11.5	3
	500	350	650	40.3	40.3	10.3	2.6
	500	700	1300	41.1	40.5	10.0	2.9
		Benzene-Acetone	Water	Benzene-Acetone	Water-Acetone	Benzene-Acetone	
Water (24 cells)	500	470	3000	37.8	4.2	0.1	2.8
	500	870	3000	36.5	9.5	1.3	2
	500	1430	3000	36.5	12	2.7	2.5
	500	1900	3000	36.5	15	2.7	3
		Benzene	Water-Acetone	Water-Acetone	Benzene-Acetone	Water-Acetone	
Water-Acetone (36 cells)	50	1400	3500	30.0	33	12.3	2.1
	145	1350	3300	30.0	33.7	12.5	2.5
	245	1450	3400	31.0	33.0	13.5	2.0
	320	1300	3700	29.0	35.0	10.7	3.5
	245	1450	3400	31.0	35.0	12.0	2.8
	305	1400	3750	30.0	36.5	12.0	3.2
	390	1400	3500	29.0	34.5	10.0	3.5
	500	1400	3750	29.0	34.5	8.4	3.7

HYDROGENATION OF DIELS-ALDER ADDUCTS OF ANTHRACENE

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The Diels-Alder condensation of anthracene with dienophiles is a reversible, temperature-dependent reaction.¹ At higher temperatures, usually above 200° C, the equilibrium is shifted in favor of the polycyclic hydrocarbon.² Pyrolysis of anthracene adducts has been suggested as a means of purifying anthracene or unsaturated alcohols.³ The low thermal stability of these adducts excludes their use as potential starting materials for the preparation of polymers. It was thought that hydrogenation of one or both benzene rings in these adducts would prevent the pyrolytic reversal reaction and produce compounds of higher thermal stability. This was found to be the case when two anthracene adducts, 9,10-dihydroanthracene-9,10-endo- α,β -succinic anhydride (I)⁴ and 11-methyl-9,10-dihydro-9,10-ethanoanthracene (VIII),⁵ were hydrogenated in the presence of ruthenium catalyst. Hydrogenation of adduct I under high pressure at 145-150° C in the presence of ruthenium-on-alumina catalyst led to the absorption of three moles of hydrogen per mole of I, producing 1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10- α,β -succinic anhydride (II).



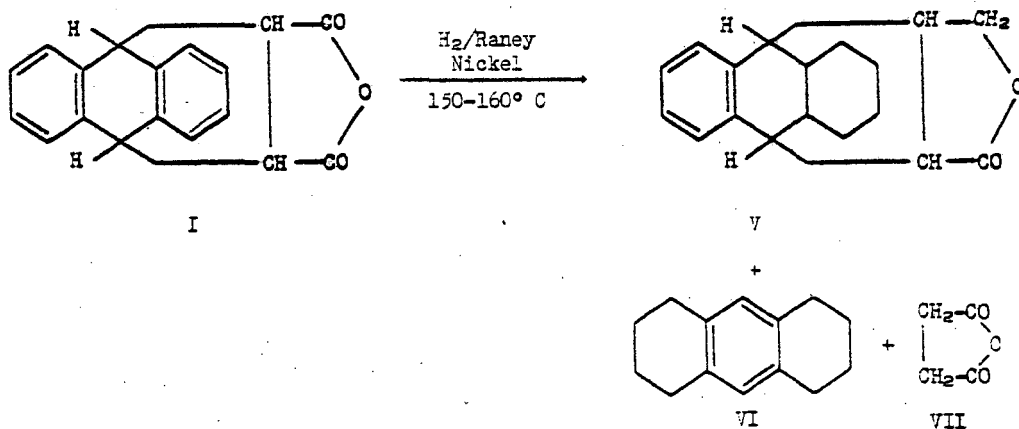
The infrared and ultraviolet spectra were consistent with structure II. The ultraviolet spectrum was that of an ortho-disubstituted benzene, and the infrared showed absorption bands characteristic of anhydride and ortho-disubstituted benzene groups.

Under the conditions employed, only one benzene ring was hydrogenated. The failure of the second benzene ring to undergo hydrogenation can be explained by steric effects as follows. The molecule of adduct I, which contains a meso-dihydroanthracene skeleton, is non-planar. It has been shown that 9,10-dihydroanthracene is bent about the line joining carbon atoms 9 and 10, each half of the molecule being planar but the two halves inclined to each other at an angle of approximately 145° .^{6,7} Assuming that addition of hydrogen to the benzene rings requires a flatwise adsorption of the unsaturated ring against the catalytic surface, it is likely that due to the bent configuration of adduct I and to the hindering effect of the bulky anhydride group, only one of the benzene rings can be hydrogenated.⁸ Inspection of the Godfrey molecular model of the adduct (I) confirms these expectations.

The hydrogenated adduct II, m.p. $145-165^\circ \text{C}$, was a mixture of stereoisomers, and no attempt was made to separate them and determine their configuration. Several derivatives of interest as potential plasticizers or pesticides, such as the diesters (III-a, b, c, d) and the N-substituted imide (IV), were prepared by standard procedures from II.

The foregoing results show that in the presence of a ruthenium catalyst, a selective hydrogenation occurred, resulting in the reduction of the aromatic ring but not affecting the succinic anhydride group of the adduct (I). In contrast, the anhydride group is attacked when a substituted succinic anhydride^{9,10} is hydrogenated in the presence of palladium or platinum catalyst, the products obtained being hydroxy-lactones, lactones, and β -methyl acids. The reduction of adduct I in the presence of Raney nickel at 160°C was also non-selective, providing a mixture of compounds. These were 1,2,3,4,4a,9,9a,10-octahydro-9,10-ethanoanthracene-11-methylol-12-carboxylic acid lactone (V), produced by an attack on the aromatic ring and the anhydride group; s-octahydroanthracene (VI); and succinic anhydride (VII).

Products VI and VII could have been formed either by hydrogenolysis or thermal decomposition of the adduct (I) followed by hydrogenation of the intermediates.



The lactone (V), m.p. $125-145^\circ \text{C}$, was a mixture of stereoisomers.

chloride were heated under reflux for 6 hours. After cooling, the precipitated diester was filtered, washed with water, and dried to yield 15.2 g. (77%) of III-a, m.p. 122-145° C, which crystallized from hexane-ethyl acetate (10:1), m.p. 145-147° C.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37.
Found: C, 73.49; H, 7.53.

Dibutyl 1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10- α,β -succinate (III-b)

A mixture of 1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10- α,β -succinic anhydride (17 g.) and n-butyl alcohol saturated with anhydrous hydrogen chloride (50 ml.) at 5° C in benzene (50 ml.) was heated under reflux for 5 hours. The cooled solution was diluted with ether and washed with 5% sodium hydroxide, then with water. After removal of the solvents, the residue was distilled to yield 21 g. (85%) of the dibutyl ester, b.p. 220-225° C (1.5 mm.), n_D^{25} 1.5710.

Anal. Calcd. for $C_{28}H_{36}O_4$: C, 75.69; H, 8.30.
Found: C, 75.13; H, 8.62.

The procedure for the preparation of other diesters was as follows: A mixture of 1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10- α,β -succinic anhydride (0.1 m.), alcohol (0.4 m.), toluene (75 ml.), and p-toluenesulfonic acid (0.5 g.) was heated at reflux until the theoretical amount of the water was collected in the trap. The cooled solution was washed with 5% sodium hydroxide, then with water, and, after removal of the solvent, the residue was distilled.

Diallyl 1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10- α,β -succinate (III-c)

b.p. 201-203° C (0.5 mm.), n_D^{25} 1.5420, 72% yield.

Anal. Calcd. for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42.
Found: C, 75.86; H, 7.62.

Di-(n-octyl)-1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10- α,β -succinate (III-d)

b.p. 245-248° C (0.4 mm.), n_D^{25} 1.5025, 88% yield.

Anal. Calcd. for $C_{34}H_{52}O_4$: C, 77.82; H, 9.99.
Found: C, 77.67; H, 10.01.

N-(2-Ethylhexyl)-1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10- α,β -succinimide (IV)

To 28.2 g. (0.1 m.) of II was added 13.5 g. (0.105 m.) of 2-ethylhexylamine, and the reaction mixture was heated with stirring to 100° C and then set aside for 2 hours. It was then heated at 160-170° C for an additional 2 hours. After removal of water by distillation, the residue was vacuum distilled to give 29.9 g. (76%) of the imide (IV), b.p. 190-232° C (0.6 mm.). On cooling, the distillate crystallized to give a product melting at 58-66° C. A sample recrystallized from petroleum ether (30-60° C) melted at 72-74° C.

Anal. Calcd. for $C_{26}H_{35}NO_2$: C, 79.34; H, 8.96; N, 3.56.
Found: C, 79.36; H, 9.08; N, 3.30.

Hydrogenation of 9,10-Dihydroanthracene-9,10- α,β -succinic Anhydride in the Presence of Raney Nickel

An "Aminco" bomb was charged with 27.6 g. of the title adduct (I), 250 ml. of ethyl alcohol, and 10 ml. of Raney nickel catalyst, and hydrogen was admitted

under 1330 p.s.i. at 25° C. The bomb was shaken and heated at 160° C for 20 hours. The amount of hydrogen absorbed corresponded to about 13.5 moles of hydrogen per mole of the starting adduct. After cooling, the solution of the hydrogenated product was separated from the catalyst by filtration, and the catalyst was washed with ether. The filtrates were combined and the solvents removed, first at atmospheric pressure, then under vacuum. The residue, composed of an oil and a solid, was treated with ethyl alcohol. The solid, insoluble in alcohol, was separated by filtration to give 4.8 g. of s-octahydroanthracene. The filtrate, after removal of the solvent by distillation, gave 20 g. of an oil.

In order to separate acidic products from non-acidic, the oil (16 g.) was heated on a steam bath with 120 ml. of 10% sodium hydroxide solution for 2 hours, and, after cooling, ether was extracted. The non-acidic product, after elimination of ether, gave an additional 5.6 g. of s-octahydroanthracene. The total of s-octahydroanthracene isolated from the reaction mixture amounted to 10.4 g., or 56%. The alkaline solution was acidified with concentrated HCl, and the precipitated solid was separated by filtration. The aqueous filtrate, after ether extraction and removal of the solvent, afforded 0.4 g. of succinic acid. The precipitated solid (6.0 g.) was crystallized several times from ethyl acetate to yield 1,2,3,4,4a,9,9a,10-octahydro-9,10-ethanoanthracene-11-methylol-12-carboxylic acid lactone, m.p. 125-145° C. Infrared absorption maxima: 5.7 (lactone) and 13.0 μ (ortho-disubstituted benzene ring).

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51.

Found: C, 79.74; H, 7.67.

Hydrogenation of 11-Methylol-9,10-dihydro-9,10-ethanoanthracene (VIII)

A mixture of 54 g. (0.228 m.) of 11-methylol-9,10-dihydro-9,10-ethanoanthracene (m.p. 105-108° C) (VIII),¹¹ 250 ml. of ethyl alcohol, and 4.0 g. of 5% ruthenium-on-alumina catalyst was placed in an autoclave, and hydrogen was admitted up to 1630 p.s.i. The vessel was shaken and heated for 6 hours at 150° C, after which the absorption of hydrogen ceased. The amount of hydrogen absorbed corresponded to about 3.8 moles of hydrogen per mole of adduct. After removal of the catalyst and solvent, the residue was distilled to yield 46 g. (84%) of a colorless oil, b.p. 150-175° C (0.6 mm.), n_D^{25} 1.5480, consisting of a mixture of 11-methylol-9,10-ethano-1,2,3,4,4a,9,9a,10-octahydroanthracene and 11-methylol-9,10-ethanoperhydroanthracene in an approximate ratio of 3 to 1.

Anal. Calcd. for $3(C_{17}H_{22}O) + C_{17}H_{28}O$: C, 83.89; H, 9.70; Molecular Weight, 244.

Found: C, 83.87; H, 10.20; Molecular Weight, 248.

(From determination of the hydroxyl content by acetylation method.)

Upon cooling, the oil partially solidified. The separated solid, 11-methylol-9,10-ethanoperhydroanthracene, crystallized from hexane, melted at 102-104° C. The infrared and ultraviolet spectra of the solid product showed complete disappearance of the aromatic ring.

Anal. Calcd. for $C_{17}H_{28}O$: C, 82.80; H, 11.36.

Found: C, 82.71; H, 11.59.

A thermal stability test of the hydrogenated adducts IX and IX + X was conducted as follows: Samples of the products were heated separately in air for 4 hours at 235-240° C. The products became colored, and according to infrared spectra, partial oxidation to the aldehydes occurred (infrared, 5.85 μ). However, no change in the carbon skeleton of the products was observed.

In a similar hydrogenation run, the crude product was separated from the catalyst, a fresh portion of the catalyst (4.0 g.) was added, and the mixture was

hydrogenated further at 160° C for an additional 17 hours. The reaction mixture contained approximately 30% of IX and 70% of X.

Acknowledgement

This work was carried out by the Coal Chemicals Research Project, sustained by the United States Steel Corporation, to whom the author is grateful for permission to publish these results.

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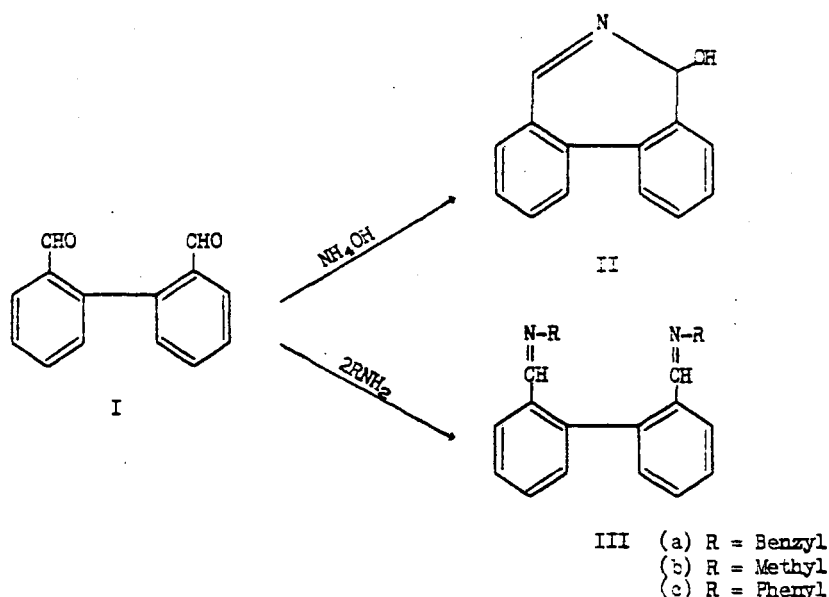
REACTIONS OF 2,2'-BIPHENYLDICARBOXALDEHYDE

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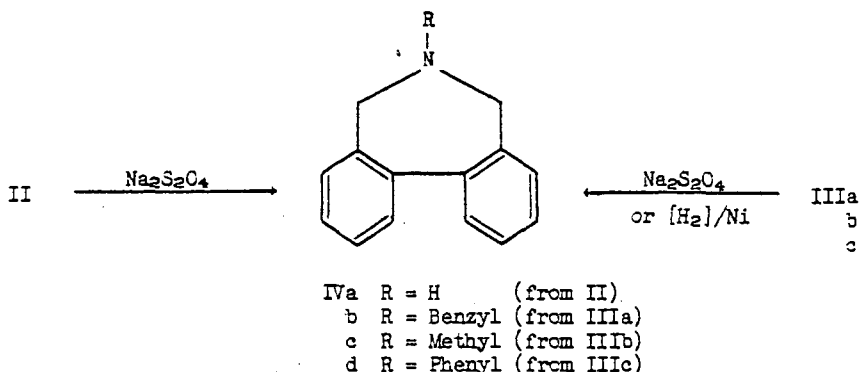
Although 2,2'-biphenyldicarboxaldehyde (I) was first reported by Kenner and Turner¹ in 1911 and later by other workers,² it has received only limited study because no simple method has existed for its preparation. Recent studies³ on the ozonolysis of phenanthrene have resulted in a relatively simple preparation of the dialdehyde from a potentially abundant starting material. The ready availability of this dialdehyde thus served as a practical stimulus to our investigation of its chemical behavior.

2,2'-Biphenyldicarboxaldehyde, I, was reacted with ammonia and primary amines to give Schiff-type bases. When I was heated with ammonium hydroxide, 5-hydroxy-5H-dibenz[c,e]azepine (II) was formed. The structure of II was assigned from elemental analysis and its infrared and NMR spectra. Infrared adsorption bands appeared at $6.15\ \mu$ ($=N=C-$) and $5.2-5.3\ \mu$ ($-C-H$). When I was reacted with benzylamine, methylamine, or aniline, 2,2'-bi(N-benzylbenzylidenimine) (IIIa), 2,2'-bi(N-methylbenzylidenimine) (IIIb), or 2,2'-bi(N-phenylbenzylidenimine) (IIIc) were the respective products. F. Mayer^{2a} reported IIIc from the reaction of N-(o-iodobenzylidene)aniline and "Naturkupper C". Infrared adsorption bands for the $=N=C-$ linkage in these compounds occurred at 6.10 to $6.15\ \mu$.



When II, IIIa, and IIIb were refluxed with aqueous sodium hydrosulfite, 6,7-dihydro-5H-dibenz[c,e]azepine (IVa) and the 6-substituted derivatives (IVb and IVc) were the respective products. Hydrosulfite reduction of 2,2'-biphenyldicarboxaldehyde monoxime also gave IVa.

Raney nickel catalyst was sufficiently active for the low-pressure hydrogenation of IIIc to IVd but not II to IVa. However, hydrogenation at higher pressure of an ethanolic solution of I and methylamine over Raney nickel yielded IVc. Low-pressure hydrogenation of I with benzylamine and methylamine over palladium catalyst gave the respective products, IVb and IVc. Only representative azepines were prepared by the various methods of reduction, and no attempt was made to study exhaustively the several different possible combinations.



It was found unnecessary to isolate the Schiff bases prior to reduction by sodium hydrosulfite. By first refluxing I with the proper amine in methanol followed by treatment with the hydrosulfite, 6-allyl (V), 6-(3-dimethylaminopropyl) (VI), 6-(3-diethylaminopropyl) (VII), and 6-(2-aminoethyl)-6,7-dihydro-5H-dibenz[c,e]azepine (VIII) were also prepared.

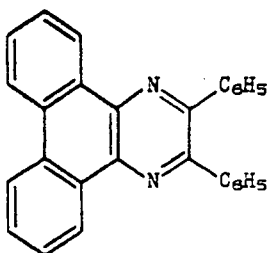
With the exception of the latter three derivatives, these 6,7-dihydroazepines had been prepared by the reaction of *o,o'*-bis(bromomethyl)biphenyl with ammonia or with primary amines.⁴ A second method involved the reaction of diphenic anhydride with ammonia to give diphenamic acid. Diphenamic acid was cyclized to diphenimide, which was in turn reduced by lithium aluminum hydride to IVa.⁵

The present method of synthesizing these azepines is superior to previous methods because of the availability of the initial starting material, phenanthrene. The yields of the azepines, isolated as acid salts, ranged from 57 to 92%.

During the present work, a British patent⁶ was granted to Hoffman-LaRoche Company for the reductive amination of the dialdehyde to azepines. However, the use of sodium hydrosulfite in reductive amination of an aldehyde appears to be novel.

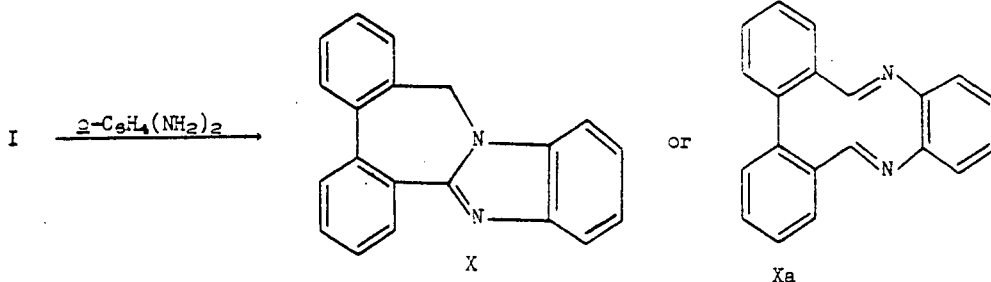
Randall and Smith⁷ screened the 6-substituted azepines for pharmacological activity and demonstrated their antipinephrine properties. V was the most effective member of the group tested.

When a solution of IIIa in *N,N*-dimethylformamide was refluxed with copper chromite, dehydrocyclization occurred to yield 2,3-diphenyldibenz[f,h]quinoxaline (IX).⁸



IX

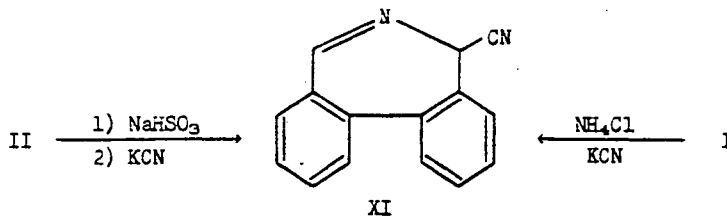
Sparatore⁹ reacted I and *o*-phenylenediamine in methanol for 48 hours and obtained a glass, m.p. 52-57° C, for which he assigned the probable structure of 15H-dibenzo[*c,e*]benzimidazo[1,2-*a*]azepine (X). An uncharacterized hydrochloride melted at 260-265° C.



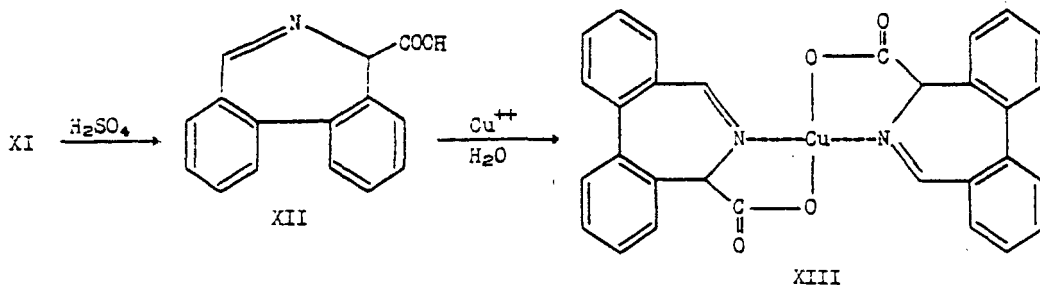
In our hands, the product from this reaction was obtained as a crystalline solid, m.p. 189-190° C, and was thought to exhibit polymorphism. Two different crystal forms were isolated which had different infrared spectra as Nujol mulls but the same spectrum in carbon disulfide and the same empirical formula. The NMR spectrum confirmed structure X rather than Xa.

A more convenient synthesis is to react the dialdehyde with *o*-phenylenediamine dihydrochloride in isopropyl alcohol, wherein the azepine precipitates presumably as the dihydrochloride monohydrate. The free base can be regenerated by treatment with alkali. The melting point of the hydrochloride is not definitive because it is believed to exist as the dihydrochloride, the monohydrochloride monohydrate, as well as the dihydrochloride monohydrate. Decomposition occurs during melting point determination, and the recorded melting point may be that of a decomposition product.

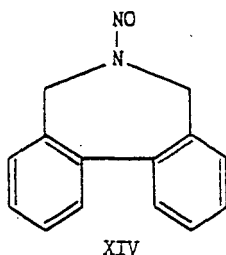
When II was treated with aqueous sodium bisulfite and then reacted with potassium cyanide, 5-cyano-5H-dibenz[*c,e*]azepine (XI) was obtained. When the dialdehyde was reacted with ammonium chloride and potassium cyanide, XI was isolated in almost quantitative yield.



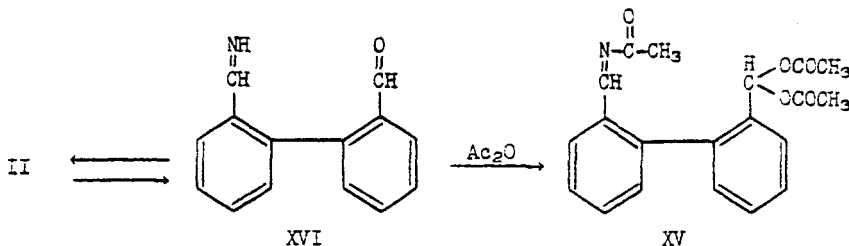
Acid hydrolysis of XI gave a product, 5H-dibenz[c,e]azepine-5-carboxylic acid (XII), which could not be sufficiently separated from inorganics for characterization. The acid complexed with metallic ions to give colored, water-insoluble chelates. The copper chelate (XIII) was characterized.



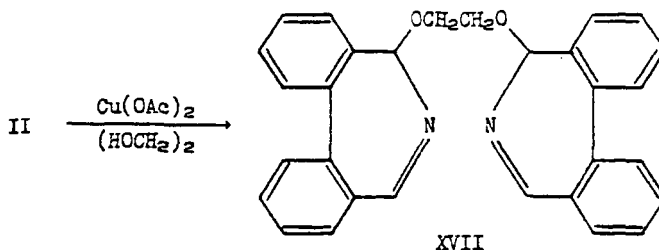
Nitrosation of IVa resulted in 6-nitroso-6,7-dihydro-5H-dibenz[c,e]azepine (XIV).



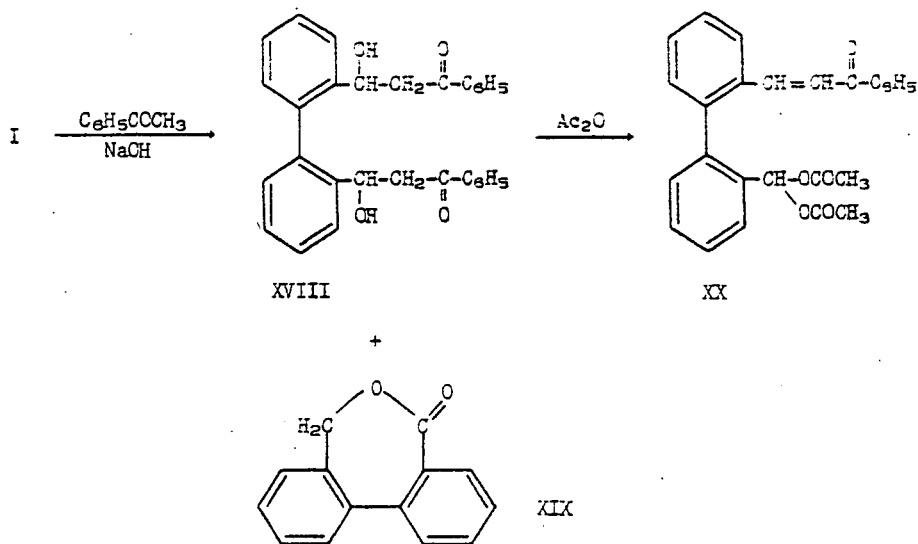
On acetylation of II by acetic anhydride, the 5-acetoxiazepine was not isolated, but rather 2-diacetoxymethyl-2'-acetyliminomethylbiphenyl (XV). The reaction might involve the isomeric structure, XVI.



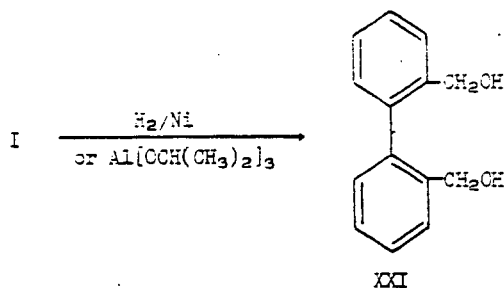
II was reacted with copper ion to give an insoluble complex, the structure of which could not be determined. However, II was reacted with ethylene glycol and cupric acetate to form 5,5'-ethylenedioxybis(5H-dibenz[c,e]azepine) (XVII). Monohydric alcohols gave oils which were not identified.



When I was reacted with two molecular equivalents of acetophenone in the presence of sodium hydroxide, a 55% yield of 2,2'-bis(1-hydroxy-2-benzoyl-ethyl)-biphenyl (XVIII) was isolated, and 2,2'-diphenide (XIX) was identified as a by-product. With an equal molecular ratio of reactants, a 35% yield of XVIII and a 57% yield of XIX, resulting from a competing Cannizzaro reaction, were isolated. Reaction of XVIII with acetic anhydride afforded 2-diacetoxymethyl-2'-(benzoylvinylene)biphenyl (XX).



2,2'-Bis(hydroxymethyl)biphenyl (XXI) was obtained from I by either catalytic hydrogenation over Raney nickel or reduction by aluminum isopropoxide. The diol has been prepared by lithium aluminum hydride reduction of dimethyl diphenate¹⁰ and diphenic acid¹¹ or by lithium borohydride reduction of dimethyl diphenate.¹²



Mayer^{2a} had prepared 9,10-phenanthraquinone by a cyanide-catalyzed benzoin-type condensation of 2,2'-biphenyldicarboxaldehyde. It was found, however, that the intramolecular condensation was also light-catalyzed, although a peroxide, such as benzoyl peroxide, was necessary as an initiator.¹³ The choice of solvent had a marked effect upon the yield of the quinone (Table I).

Table I

Yield of Phenanthraquinone Obtained from Irradiation
of 2,2'-Biphenyldicarboxaldehyde in Various Solvents

<u>Solvent</u>	<u>Yield of Phenanthraquinone, %</u>	<u>Reaction Conditions</u>
t-Butyl Alcohol	5	Irradiation (Mercury Arc) for 48 hours at room temperature; 3 hours at reflux. One weight per cent benzoyl peroxide catalyst.
Acetic Acid	15	
Benzene	5	
Ethyl Ether	0	
Tetrahydrofuran	0	
Xylene	0	
Acetone	32	

The yield in acetone was increased from 32% to 50% by reflux for 72 hours. The remaining material was unreacted dialdehyde.

Experimental¹⁴

5-Hydroxy-5H-dibenz[c,e]azepine (II). Four grams of I was refluxed with 28% ammonium hydroxide (60 ml.) for 15 min. The mixture was cooled, and the colorless 5-hydroxy-5H-dibenz[c,e]azepine (3.7 g.; 97%), m.p. 126.8-128.8° C, was collected.

Anal. calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.20; N, 6.70. Found: C, 80.59; H, 5.59; N, 7.00.

2,2'-Bi(N-benzylbenzylidenimine) (IIIa). I (2.1 g.; 0.01 mole), dissolved in toluene (30 ml.), was refluxed with benzylamine (2.20 ml.; 0.02 mole) for 15 min. The toluene was evaporated under reduced pressure, leaving an oil. Trituration with water afforded the solid 2,2'-bi(N-benzylbenzylidenimine) (3.86 g.; 99%), m.p. 94-97° C. Recrystallization from n-heptane gave crystals with a m.p. of 96-97° C.

Anal. calcd. for $C_{28}H_{24}N_2$: C, 86.56; H, 6.23; N, 7.21. Found: C, 86.53; H, 6.25; N, 7.21.

2,2'-Bi(N-methylbenzylidenimine) (IIIb). I (4.2 g.; 0.02 mole) was heated at 75-80° C in 15% aqueous monomethylamine (45 ml.) for 1 hr. with stirring. The colorless crystals (4.66 g.; 98%), m.p. 144-146° C, were collected. Recrystallization from n-heptane gave the pure 2,2'-bi(N-methylbenzylidenimine), m.p. 151.0-152.2° C.

Anal. calcd. for $C_{18}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.86. Found: C, 81.32; H, 6.84; N, 11.84.

2,2'-Bi(N-phenylbenzylidenimine) (IIIc). I (2.1 g.; 0.01 mole) and aniline (2.04 g.; 0.021 mole) were refluxed in toluene (30 ml.) for 2 hr., with water being collected in a Dean-Stark trap. After evaporation of the toluene, the residue was dissolved in boiling n-heptane and the solution cooled. Light-yellow crystals (3.22 g.; 89%) of 2,2'-bi(N-phenylbenzylidenimine), m.p. 95.4-97.2° C, were obtained. Further recrystallization from n-heptane gave the pure compound, m.p. 97.6-99.0° C (lit., 98-99° C).^{2a}

6,7-Dihydro-5H-dibenz[c,e]azepine (IVa), Method A. II (3.0 g.) and sodium hydrosulfite (9.0 g.) were refluxed in water (100 ml.) for 30 min. On cooling the solution, colorless crystals separated and were collected. Additional material was separated by adding sodium chloride to the filtrate. The combined solids were dissolved in water (200 ml.) containing concentrated hydrochloric acid (20 ml.), and the solution was refluxed for 30 min. After concentrating the solution to 50 ml. and cooling,

6,7-dihydro-5H-dibenz[c,e]azepine hydrochloride (3.0 g.; 92%), m.p. 290.2-291.2° C (lit., 286-288° C),^{4b} separated.

Method B. I (2.1 g.; 0.01 mole) in methanol (30 ml.) was added to a solution of hydroxylamine hydrochloride (0.7 g.; 0.10 mole) in water (300 ml.). The precipitated 2,2'-biphenyldicarboxaldehyde monoxime (2.0 g.; 91%), m.p. 97-99° C, was collected.

Anal. calcd. for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.21. Found: C, 74.63; H, 4.96; N, 6.30.

The monoxime (1.0 g.; 0.005 mole) and sodium hydrosulfite (4.0 g.; 0.023 mole) were refluxed in water (50 ml.) for 30 min. The solid which separated on cooling was collected and refluxed for 30 min. in 10% hydrochloric acid (50 ml.). The solution was cooled and neutralized with sodium bicarbonate to precipitate 6,7-dihydro-5H-dibenz[c,e]azepine (0.7 g.; 31%), m.p. 38-93° C. Since the amine had not been reported as a solid, it was dissolved in ethyl ether, and the hydrochloride, m.p. 290-291° C, precipitated with hydrogen chloride. The infrared spectrum was identical to that of the product from Method A.

6-Benzyl-6,7-dihydro-5H-dibenz[c,e]azepine (IVb). I (2.1 g.; 0.01 mole) and benzylamine (1.6 ml.; 0.015 mole) were refluxed in toluene (15 ml.) for 1 hr. Water of reaction was collected in a Dean-Stark trap. The toluene was removed under an air blast, and the remaining oil, dissolved in methanol, was refluxed for 45 min. with sodium hydrosulfite (10 g.) in water (50 ml.). The methanol was distilled from the mixture and the cooled aqueous phase decanted from the semisolid material. The latter was refluxed with 3% hydrochloric acid (100 ml.) and the solution filtered. The cooled filtrate was made basic (pH 12) with sodium hydroxide. The precipitated oil was extracted into ether and the ether dried over potassium hydroxide pellets. Anhydrous hydrogen chloride was passed into the ether until the precipitation of 6-benzyl-6,7-dihydro-5H-dibenz[c,e]azepine hydrochloride hemihydrate (2.99 g.; 87%), m.p. 203-205° C (lit., 205° C),^{4c} was complete.

Methiodide. 6-Methyl-6-benzyl-6,7-dihydro-5H-dibenz[c,e]azepinium iodide, m.p. 136-138° C (lit., 138-139° C).^{4b}

6-Methyl-6,7-dihydro-5H-dibenz[c,e]azepine (IVc). I (4.2 g.; 0.02 mole) was heated at 85° C with stirring in 30% monomethylamine (25 ml.) for 30 min. The 2,2'-bi(N-methylbenzylidenimine) was collected and boiled with sodium hydrosulfite (12 g.) and water (75 ml.) for 30 min., allowing the volume to be reduced to 20 ml. When cool, the aqueous phase was decanted from the semisolid product. After washing and drying, this material was dissolved in n-heptane, and anhydrous hydrogen chloride was passed into the solution until precipitation of 6-methyl-6,7-dihydro-5H-dibenz[c,e]azepine hydrochloride (4.0 g.; 81%), m.p. 221-224° C, was complete.

Methiodide. 6,6-Dimethyl-6,7-dihydro-5H-dibenz[c,e]azepinium iodide, m.p. 287-289° C (lit., 287-288° C).^{4c}

Hydrogenation. A solution of I (0.0238 mole) and two molecular equivalents of the appropriate amine in ethanol (35 ml.) with the appropriate catalyst (10% on the dialdehyde) was subjected to hydrogenation in a low-pressure (50-60 p.s.i.g.) autoclave (Parr Instrument Company) or in a Magne-Dash autoclave (Autoclave Engineers) at higher pressures. After hydrogenation and removal of catalyst and solvent, the residue was refluxed with water (300 ml.) and sufficient hydrochloric acid to give pH 2. Any unreacted dialdehyde was collected by filtration, and the filtrate was concentrated to allow crystallization of the azepine hydrochloride.

Product	Catalyst	Hydrogen Pressure, p.s.i.g.	Temperature, °C	Time, hr.	Yield, %	m.p., °C
IVa	Raney Ni	850	75	17	51	287-290
IVa	5% Pt on Carbon	800	85	24	84	284-290
IVb	5% Pd on Carbon	60	50	18	91	202-208
IVc	5% Pd on Carbon	60	50	7	97	221-227

6-Phenyl-6,7-dihydro-5H-dibenz[c,e]azepine (IVd). 2,2'-Bi(N-phenylbenzylidenimine) (2.27 g.) in ethanol (50 ml.) was hydrogenated over Raney nickel (0.1 g.) at room temperature and 50 p.s.i. pressure for 7 hr. After removal of catalyst and evaporation of the ethanol, the semisolid product was crystallized from *n*-heptane to give 6-phenyl-6,7-dihydro-5H-dibenz[c,e]azepine (1.3 g.; 76%), m.p. 37-90° C. Upon recrystallization, the m.p. was 89.5-91.6° C.

Anal. calcd. for $C_{20}H_{17}N$: N, 5.17. Found: N, 5.38.

6-Allyl-6,7-dihydro-5H-dibenz[c,e]azepine (V). I (4.2 g.; 0.02 mole) and allylamine (3.1 ml.; 0.041 mole) were refluxed in methanol for 5 min. A solution of sodium hydrosulfite (15 g.) in water (75 ml.) was added to the cooled solution and the mixture refluxed for 30 min. After distilling over the methanol, the suspended oil was extracted into ethyl ether from the cooled aqueous phase. After drying the ether extract over potassium hydroxide, crude 6-allyl-6,7-dihydro-5H-dibenz[c,e]azepine hydrochloride (4.88 g.; 90%), m.p. 190-200° C, was precipitated by hydrogen chloride. Recrystallization from methanol-ethyl ether gave a 57% yield, m.p. 214-215° C (lit., 214-215° C).^{4a}

6-(3-Dimethylaminopropyl)-6,7-dihydro-5H-dibenz[c,e]azepine (VI). Dimethylaminopropylamine (Union Carbide Chemicals Company) (4.90 g.; 0.048 mole) was added to a solution of I (10 g.; 0.048 mole) in methanol (15 ml.). After 5 min., a solution of sodium hydrosulfite (30 g.) in water (330 ml.) was added and the solution refluxed for 1 hr. After removing two-thirds of the solvent by distillation, 10% aqueous sodium hydroxide (75 ml.) was added to the cooled solution to precipitate the azepine as an oil. The oil was extracted into ethyl ether. The ether phase was washed well with water, separated, and evaporated from the amine. The azepine was dissolved in isopropyl alcohol and reacted with excess hydrogen chloride. Crystalline 6-(3-dimethylaminopropyl)-6,7-dihydro-5H-dibenz[c,e]azepine dihydrochloride monohydrate, m.p. 227-230° C (dec.), separated from the solution. The yield was 10.9 g. (62%). This material was recrystallized from isopropyl alcohol to a m.p. of 231.2-232.3° C (dec.).

Anal. calcd. for $C_{19}H_{24}N_2 \cdot 2HCl \cdot H_2O$: C, 61.45; H, 7.60; Cl, 19.10; N, 7.55. Found: C, 61.29; H, 7.91; Cl, 18.64; N, 7.35.

6-(3-Diethylaminopropyl)-6,7-dihydro-5H-dibenz[c,e]azepine (VII). The 6-(3-diethylaminopropyl) derivative was prepared similarly to the previous compound. The dihydrochloride was too deliquescent for easy handling, so the diphosphate was prepared by dissolving the amine in methanol (40 ml.) and 85% phosphoric acid (8.5 g.). After crystallization was complete, 17.4 g. (70% yield) of 6-(3-diethylaminopropyl)-6,7-dihydro-5H-dibenz[c,e]azepine diphosphate monohydrate, m.p. 220-223° C (dec.) (lit., 220-222° C),⁸ was obtained. After recrystallization from ethanol-water, the pure compound melted at 221.5-223.5° C (dec.).

Anal. calcd. for $C_{21}H_{28}N_2 \cdot 2H_3PO_4 \cdot H_2O$: C, 48.27; H, 6.94; N, 5.36. Found: C, 48.82; H, 6.72; N, 5.19.

6-(2-Aminoethyl)-6,7-dihydro-5H-dibenz[c,e]azepine (VIII). Ethylenediamine (2.0 ml.; 0.02 mole) was added to a solution of I (4.2 g.; 0.02 mole) in methanol at room temperature. After 5 min., sodium hydrosulfite (10 g.) in water (50 ml.) was added and the mixture refluxed for 1 hr. After cooling, the aqueous phase was decanted and the residue refluxed with 5% aqueous sodium hydroxide (20 ml.) and toluene

(20 ml.) for a few minutes, dissolving the product in the toluene layer. The organic phase was separated, washed with water, and dried over potassium hydroxide pellets. The crude 6-(2-aminoethyl)-6,7-dihydro-5H-dibenz[c,e]azepine dihydrochloride (4.6 g.; 74%), m.p. 225-260° C, was precipitated by hydrogen chloride. Recrystallization from methanol gave the pure compound (3.9 g.; 63%), m.p. 268-270° C.

Anal. calcd. for $C_{16}H_{18}N_2 \cdot 2HCl$: C, 61.73; H, 6.47; N, 9.00. Found: C, 61.42; H, 6.29; N, 9.38.

2,3-Diphenyldibenz[f,h]quinoxaline (IX). I (5.0 g.) and benzylamine (5.1 g.) were refluxed in toluene (20 ml.) for 30 min. The water of reaction was collected in a Dean-Stark trap. After evaporation of the toluene, the residual oil, in N,N-dimethylformamide (35 ml.), was refluxed with powdered copper chromite (0.5 g.) for 2 hr. After removal of catalyst and solvent, the oily residue was triturated with methanol (15 ml.). The insoluble portion (1.5 g.), m.p. 260-265° C, was crystallized from benzene to give crystals (1.4 g.; 15%), m.p. 272-275° C (lit., 272° C).¹⁵

15H-Dibenzo[c,e]benzimidazo[1,2-a]azepine (X), Method A. A solution of I (2.10 g.) and *o*-phenylenediamine (1.08 g.) in methanol (40 ml.) remained at ambient temperature for 48 hr. After removal of the solvent by vacuum evaporation, a benzene (25 ml.) solution of the residual oil was absorbed on a column (2 x 16 cm.) of neutral alumina (Bio Rad AG7, 100-200 mesh). Elution with benzene gave 2.35 g. of a solid, m.p. 135-150° C. Recrystallization from benzene gave the product (1.37 g.; 50%), m.p. 169-190° C. Picrate, 279-281° C (dec.) (lit., 278-280° C).⁹

Anal. calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 4.99; N, 9.93. Found: C, 85.08; H, 5.34; N, 10.15.

NMR: The chemical shift value for the aliphatic protons was 5.03 τ (area ratio: aromatic to aliphatic protons, 5.5; theory, 6.0). A comparison of 1.82 τ for the methine proton in salicaldoxime and 6.38 τ for the methylene protons adjacent to the phenyl group in N,N,N',N'-tetrabenzylmethylene diamine¹⁶ led to the assignment of structure X rather than structure Xa.

The dialdehyde (2.10 g.) and *o*-phenylenediamine dihydrochloride (1.81 g.), dissolved in methanol (25 ml.) (a deep-red solution), were heated at reflux for 20 min. (red color was discharged). The volume was reduced by one-half and the mixture cooled. The crystals thus formed (2.36 g.), m.p. 252-256° C beginning at ambient temperature, were collected. If a sample were introduced into the melting point block at 240° C, the sample melted with gas evolution, solidified, and remelted at 252-256° C. The infrared spectrum contained peaks at 2.8 μ , 3.8 μ , and 4.3 μ . Thus the composition $X \cdot 2HCl \cdot H_2O$ was assigned. A sample of the above, heated at 140° C under vacuum, lost 4.34% in weight (theory for $1H_2O$: 4.83%) and now melted at 256-260° C. The 2.3 μ peak was now missing in the infrared spectrum of the dihydrochloride. $X \cdot 2HCl$ (1.0 g.) was recrystallized from isopropyl alcohol (25 ml.) and water (1 ml.). The crystals (0.5 g.) now melted at 263-267° C when placed in the apparatus at 240° C (m.p. 240-245° C from ambient temperature). The infrared spectrum now contained peaks at 2.3 μ and 3.8 μ but none at 4.3 μ , giving support to the composition $X \cdot HCl \cdot H_2O$.

Anal. calcd. for $C_{20}H_{14}N_2 \cdot HCl \cdot H_2O$: N, 8.32; Cl, 10.53. Found: N, 8.40; Cl, 10.40.

Method B. I (2.10 g.; 0.01 mole) and *o*-phenylenediamine dihydrochloride (1.81 g.; 0.01 mole) in isopropyl alcohol (50 ml.) were refluxed for 2 hr. The reaction mixture was cooled to 0° C and filtered. The residue (2.34 g.) was washed with cold isopropyl alcohol (10 ml.) and dried. The hydrochloride was dissolved in boiling 95% ethanol (30 ml.), and water (60 ml.) was added. The solution was made alkaline (pH 8) with aqueous 20% sodium hydroxide solution. The azepine base separated. After concentrating to one-half of the volume, the free base was collected. The yield was

1.99 g. (70%) of buff-colored product melting at 185-188° C. Crystallization from benzene gave rhomboid-like crystals, m.p. 186-189° C. Recrystallization from *n*-heptane gave mixed crystals, which on repeated recrystallization from *n*-heptane gave solely a needle form, m.p. 189-192° C.

Anal. calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 4.99; N, 9.93. Found: C, 85.26; H, 5.28; N, 10.19.

The needle form of X could be reconverted to the rhomboid form by dissolving in methanol, evaporating to an oily semisolid, and crystallizing from ethyl acetate. A few repetitions of this process gave solely the rhomboid form of X, m.p. 188-191° C.

Anal. calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 4.99; N, 9.93. Found: C, 85.24; H, 5.05; N, 9.85.

Comparison of the infrared spectra of the two forms in Nujol mulls showed sufficient dissimilarity to suggest polymorphism. The rhomboid form showed bands at 6.2 μ and 14.1 μ , which were absent in the needle form. The needle form showed bands at 10.8 μ and 11.9 μ , which were absent in the rhomboid form. Solution infrared spectra of the crystal forms in carbon bisulfide were identical, with no absorption at the above wave lengths.

5-Cyano-5H-dibenz[c,e]azepine (XI), Method A. A solution of II (6.3 g.; 0.03 mole) in acetic acid (30 ml.) was added to a solution of sodium bisulfite (3.1 g.; 0.03 mole) in water (75 ml.) and evaporated to dryness. A solution of potassium cyanide (1.9 g.; 0.03 mole) in water (30 ml.) was added to the residue dissolved in water (200 ml.). The solution was heated at 90° C for 1 hr. 5-Cyano-5H-dibenz[c,e]-azepine (5.0 g.; 82%), m.p. 150-152° C, precipitated. Recrystallization from ethyl acetate-*n*-heptane gave a m.p. of 154-156° C.

Anal. calcd. for $C_{15}H_{10}N_2$: C, 82.56; H, 4.62; N, 12.83. Found: C, 82.46; H, 5.21; N, 12.84.

Method B. A solution of I (21.0 g.; 0.1 mole) in methanol (300 ml.) was slowly poured into water (3 l.) containing ammonium chloride (16 g.; 0.33 mole) and potassium cyanide (6.5 g.; 0.01 mole). The solution was refluxed for 30 min. and cooled. The 5-cyano-5H-dibenz[c,e]azepine (20 g.; 99%), m.p. 150-153° C, was collected, washed with water, and dried.

5H-Dibenz[c,e]azepine-5-carboxylic Acid (XII). 5-Cyano-5H-dibenz[c,e]azepine (2.6 g.; 0.012 mole) was refluxed for 2 hr. in 67% sulfuric acid (50 ml.). The cooled reaction solution was poured into cold water (100 ml.) containing sodium hydroxide (34.6 g.). The pH of the solution was then adjusted to 6.8, and the solids, consisting of the product and sodium sulfate, which separated were collected and dried. 5H-Dibenz[c,e]azepine-5-carboxylic acid was extracted from the solid into hot methanol. Evaporation of the methanol gave 2.4 g. (87%) of the acid, m.p. 249-253° C. Since the acid was difficult to free of sodium sulfate, an analytical sample was prepared in the form of a water-insoluble copper chelate, XIII. A solution of copper sulfate pentahydrate (0.628 g.; 0.0025 mole) in water (25 ml.) was added to a solution of the acid (1.1 g.; 0.005 mole) in water (25 ml.). The lavender-colored complex (1.2 g.), m.p. 221-222° C, which precipitated was collected, washed, and dried.

Anal. calcd. for $(C_{15}H_{10}NO_2)_2Cu \cdot 2H_2O$: C, 62.98; H, 4.22; Cu, 11.10; H_2O , 6.29. Found: C, 63.10; H, 4.20; Cu, 10.77; H_2O , 6.12.

6-Nitroso-6,7-dihydro-5H-dibenz[c,e]azepine (XIV). Sodium nitrite (2.8 g.; 0.04 mole) was added to a solution of 6,7-dihydro-5H-dibenz[c,e]azepine hydrochloride (2.0 g.; 0.009 mole) in water (150 ml.) and hydrochloric acid (2.0 ml.). 6-Nitroso-6,7-dihydro-5H-dibenz[c,e]azepine (1.8 g.; 93%), m.p. 107-112° C (dec.), which crystallized from solution, was collected and dried.

Anal. calcd. for $C_{14}H_{12}N_2O$: C, 75.00; H, 5.36; N, 12.50. Found: C, 74.90; H, 5.55; N, 12.53.

2-Diacetoxymethyl-2'-acetylaminobiphenyl (XV). II (2.3 g.) was refluxed in acetic anhydride (50 ml.) for 30 min. After removing the excess acetic anhydride by vacuum distillation, the crude product (3.5 g.), m.p. 132-160° C, was washed with ethyl acetate (15 ml.). The undissolved material was 2-diacetoxymethyl-2'-acetylaminomethylbiphenyl (2.0 g.; 51%), m.p. 177-181° C. Recrystallization from ethyl acetate gave the pure compound, m.p. 184-186° C.

Anal. calcd. for $C_{20}H_{18}NO_5$: C, 67.97; H, 5.42; N, 3.98. Found: C, 67.81; H, 5.40; N, 4.26.

5,5'-Ethylenedioxybis(5H-dibenz[c,e]azepine) (XVII). Cupric acetate monohydrate (7.5 g.; 0.038 mole) was added to a solution of II (15 g.; 0.072 mole) in ethylene glycol (150 ml.) and water (30 ml.) and the mixture refluxed for 1.5 hr. Precipitated cupric hydroxide was removed by filtration and chloroform added to the filtrate. The chloroform was washed with 7% aqueous sodium bicarbonate (300 ml.) and then with water. After separation, the chloroform layer was evaporated to a volume of 200 ml., and n-heptane was added to cause crystallization of the crude product (11.7 g.; 71%), m.p. 227-232° C. Recrystallization from chloroform-acetone gave the pure compound, m.p. 244-246° C.

Anal. calcd. for $C_{30}H_{24}N_2O_2$: C, 80.96; H, 5.44; N, 6.30. Found: C, 80.79; H, 5.58; N, 6.26.

2,2'-Bis(1-hydroxy-2-benzoylethyl)biphenyl (XVIII). A solution of sodium hydroxide (2.1 g.) in water (80 ml.) was added to a solution of I (4.6 g.; 0.022 mole) in ethanol (80 ml.). Acetophenone (5.2 g.; 0.044 mole) was added to the resulting solution over a 1-min. period. Colorless crystals soon formed and after only several minutes were collected, washed with ethanol (-5 to 0° C), and dried. This crude 2,2'-bis(1-hydroxy-2-benzoylethyl)biphenyl weighed 5.5 g. (55%), m.p. 175-185° C. Recrystallization from methanol gave the pure compound, m.p. 238.5-239.0° C (dec.).

Anal. calcd. for $C_{30}H_{28}O_4$: C, 79.75; H, 5.81. Found: C, 79.74; H, 5.69.

The use of one molar equivalent of acetophenone as above gave 35% yield of XVIII and 57% yield of diphenide, m.p. 124-130° C (lit., 132° C).¹ The infrared spectrum was identical with that of authentic diphenide.

2-Diacetoxymethyl-2'-(benzoylvinylen)biphenyl (XX). 2,2'-Bis(1-hydroxy-2-benzoylethyl)biphenyl (6.0 g.) was refluxed in acetic anhydride (100 ml.) for 1 hr. The acetic anhydride was removed by flash evaporation. The residual oil was dissolved in ethanol, from which, on concentration, 3.9 g. (70%) of crude 2-diacetoxymethyl-2'-(benzoylvinylen)biphenyl, m.p. 197-204° C, was obtained. Recrystallization from ethyl acetate gave the pure compound, m.p. 208.5-209.5° C.

Anal. calcd. for $C_{28}H_{22}O_5$: C, 75.30; H, 5.36; N, 19.34. Found: C, 74.92; H, 5.46; N, 19.62.

2,2'-Bis(hydroxymethyl)biphenyl (XXI), Method A. Aluminum isopropoxide (2.8 g.; 0.014 mole) was mixed with anhydrous isopropyl alcohol (100 ml.) containing I (4.2 g.; 0.02 mole). Acetone was distilled from the reaction through a 12-in. Vigreux column followed by the majority of the isopropyl alcohol. The cooled reaction mixture was poured into 20% hydrochloric acid (100 ml.). The precipitated 2,2'-bis(hydroxymethyl)biphenyl (4.01 g.), m.p. 92-100° C, was collected, washed, and dried. Recrystallization from benzene gave 2.79 g. (65%) of material melting at 109.4-109.8° C (lit., 112-113° C).¹⁰

Method B. I (15 g.) in ethanol (100 ml.) was hydrogenated (50 p.s.i.) over Raney nickel catalyst (0.5 g.) at 52° C for 18 hr. After removal of the catalyst by filtration, the ethanol was flash evaporated and the residue recrystallized from benzene to give 12.4 g. (81%) of 2,2'-bis(hydroxymethyl)biphenyl, m.p. 109.0-109.8° C.

9,10-Phenanthraquinone. A solution of I (2.1 g.; 0.01 mole) in acetone (100 ml.) containing benzoyl peroxide (0.02 g.) was refluxed for 72 hr. with continuous irradiation from a mercury vapor lamp (Hanovia Chemical and Manufacturing Company, Type 16200; filter removed) at a distance of 5-6 in. The solution was aerated at the rate of approximately 0.06 S.C.F.M. The acetone was flash evaporated, and a 50% yield of 9,10-phenanthraquinone, m.p. 196-206° C (lit., 206-207° C),¹⁷ was recovered by washing the residue with ethyl ether. The material dissolved in the ether was largely unchanged dialdehyde, identified by an infrared spectrum.

Other solvents—i-butyl alcohol, acetic acid, benzene, ethyl ether, tetrahydrofuran, and xylene—were employed similarly, except that the reaction time was 48 hr. at room temperature followed by 3 hr. at reflux.

Acknowledgement

The authors wish to express their gratitude to the United States Steel Corporation, Sponsor of the Coal Chemicals Research Project at Mellon Institute, for the permission to publish these results. The assistance of Mr. J. R. Harris in the obtaining of infrared spectra is gratefully acknowledged.

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